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Reactions of Free Radicals with Organic Cations

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The kinetics and mechanisms of the reactions of organic cations of different types with neutral radicals, radical-anions, and radical-cations are considered and the dependences of the rates of these reactions on the nature of the substituents in the reactants, the charges on the radicals, the nature of the solvents and counterions, and the presence of crown ethers are analysed. The applications of the reactions of cations with radicals in the alkylation and arylation of organic compounds, in diazotypes, and in cationic and radical polymerisation are briefly surveyed.
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I. INTRODUCTION

As early as the beginning of the 1940's, the interaction of free radicals with diazonium cations was postulated[1,2] to account for the formation of azobenzenes in the reduction of diazonium salts. It was later established that the dediazotisation processes in methanol,[3-10] hypophosphorous acid,[11,12] and cyclic ethers[13,14] proceed via a radical-chain mechanism and that diazonium cations interact with radicals in the chain propagation and termination stages. Subsequent studies showed that the reactions of radicals with organic cations are very common in organic chemistry and are important in organic synthesis, in the electrochemistry of organic compounds, in polymer chemistry, and in diazotypes. Their kinetics and mechanisms have a number of characteristic features of general interest for the chemistry of organic cations and free radicals. The present review is devoted to the analysis and survey of the available literature data on the kinetics and mechanisms of the reactions of organic cations with neutral radicals, radical-anions, and radical-cations and their practical applications.

II. REACTIONS WITH DIAZONIUM CATIONS

Reactions of radicals with diazonium cations have been most thoroughly investigated. Various processes involving the thermal, photochemical, and radiation-chemical reduction of these cations result in the formation of aryl radicals, which can interact with the initial cations or can abstract hydrogen atoms from solvent molecules, forming radicals which also react with the cations. It has been suggested that the attack by radicals can be directed to the aromatic nucleus of the cation or to the diazo-group. The reactions of the first type account for the formation of arylazobenzenes, for example, in the reduction of diazonium salts by potassium hexacyanoferrate(II) in water.[2] The following reaction mechanism has been proposed:[2]

$$RC_6H_4^{\cdot} + RC_6H_4N_2^{+} \rightarrow RC_6H_4C_6H_4(R)N_2^{+} \quad (1)$$

$$RC_6H_4C_6H_4(R)N_2^{+} + RC_6H_4^{\cdot} \xrightarrow{-H^{+}} RC_6H_4C_6H_3(R)N{=}N{-}C_6H_4R \quad (2)$$

Among the products of the chain reaction of methanol with p-$ClC_6H_4N_2^{+}BF_4^{-}$, initiated by γ-radiation in water, the isomers of dichlorobiphenyl were isolated.[15] The authors suggest that these are formed as a result of reactions of type (I) and subsequent reduction of the radical-cation and the elimination of nitrogen. The isotopic composition of the biphenyl, formed on treatment of $PhN_2^{+}Cl^{-}$ with an aqueous solution of alkali in deuteriated benzene, has been explained[16] on the basis of a reaction mechanism involving the addition of the phenyl radical to the aromatic nucleus of the diazonium ion as one of the stages. However, we may note that the attack by radicals on the aromatic nucleus of the diazonium cation has not been unambiguously demonstrated, as the products of the above reactions can also be obtained in a different way.

The attack by the radicals on the diazo-group, i.e.

$$Ar^{\cdot} + ArN_2^{+} \rightarrow ArN{=}NAr^{+} \xrightarrow{e^{-}} ArN{=}NAr \quad (3)$$

has been proposed by Waters[1] to account for the formation of symmetrical azobenzenes in the Sandmeyer reaction. However, these azo-compounds can be obtained as a result of the recombination of aryl and diazenyl radicals and direct evidence for the formation of the radical-cations derived from azo-compounds was not obtained in Waters' studies.

Such evidence was obtained appreciably later in the study of the EPR spectra of the products of the benzenediazonium cation with sodium dithionate.[17,18] The authors observed in the EPR spectrum a quintet corresponding to the interaction of the unpaired electron with two equivalent nitrogen nuclei ($a_{N(1)} = a_{N(2)} = 9.2$ G). The g-factor for the radical was 2.0035. The observed spectrum was initially erroneously attributed to the diazenyl radical $C_6H_5N_2$. However, quantum-chemical calculation for the latter demonstrated[19] that it is a σ-radical in the ground state and that its nitrogen atoms are non-equivalent: $a_{N(1)} = 5.8$ G and $a_{N(2)} = 14.6$ G. This result agrees well with the hyperfine interaction (HFI) constants for diazenyl radicals obtained on decomposition of benzeneazoalkanes. It has been concluded[19] that the EPR spectrum obtained in the earlier studies[17,18] corresponds to the azobenzene radical-cation, since the calculated[19] and experimental[17,19] HFI constants for the nitrogen atoms in this radical-cation were found to agree.

On the basis of the dependence of the radiation-chemical yield in the consumption of the salt p-$CH_3C_6H_4N_2^{+}BF_4^{-}$ on its concentration in the chain decomposition process initiated by γ-radiation in aqueous methanol solution, it has been suggested[15] that chain termination proceeds via reaction (3) and the rate constant for this reaction was calculated ($k = 4.2 \times 10^6$ litre mol^{-1} s^{-1}).

It has been suggested[19] that not only aryl but also many other radicals can react via mechanism (3). The first evidence for this was obtained in relation to the radicals generated by the abstraction of hydrogen atoms from β-carbon atoms in alcohols or aldehydes by aryl radicals in the chain decomposition reaction of p-$CH_3C_6H_4N_2^+BF_4^-$ initiated by γ-radiation in aqueous solutions of ethanol, isopropyl alcohol, or aldehydes (RH_2). The reaction rate constants were determined from kinetic data:

$$\beta\text{-}RH^{\cdot} + p\text{-}CH_3C_6H_4N_2^+ \rightarrow p\text{-}CH_3C_6H_4N{=}N{-}\beta\text{-}RH^+ \qquad (4)$$

They proved to be 1.1×10^4 and 3.8×10^4 litre mol^{-1} s^{-1} for the radicals $HOCH_2CH_2^{\cdot}$ and $HOCH(CH_3)CH_2^{\cdot}$ respectively.[20]

The influence of substituents in the nucleus of the diazonium cation on the rate of reaction (4) with β-radicals of isopropyl alcohol has been investigated.[15] It was found that the values of $\lg k_4$ are correlated with the σ^+ constants of the substituents in the cation: $\rho_+ = -0.5$ for the substituents p-CH_3O, p-CH_3, and p-Cl, while the inclusion of p-CN and p-NO_2 in this series lowers ρ_+ to −1.0. The acceleration of the reaction following an increase in the electron-donating capacity of the substituent has been explained[15] by the stabilisation of the electron-deficient radical-cation when substituents are introduced into the nucleus.

By analogy with the azo-coupling reaction, the addition of radicals to the diazo-group and subsequent reduction of the radical-cations to neutral azo-compounds were called the free-radical azo-coupling reaction.[21-23] This reaction became a convenient method of synthesis of alkylaryldiazenes, especially those with tertiary alkyl residues:

$$R^{\cdot} + ArN_2^+ \rightarrow R{-}N{=}N{-}Ar^+ \xrightarrow{M^{n+}} R{-}N{=}N{-}Ar + M^{(n+1)+}$$
$$M^{n+} = Ti^{3+},\ Fe^{2+} \qquad (5)$$

The radicals $R^{\cdot}$ are generated either in the reactions of aryl radicals with alkyl iodides or in the reactions of ketones or dialkyl sulphoxides with hydrogen peroxide in the presence of iron(II) salts. The yield of azo-compounds is 30–80% of theoretical depending on the nature of $R^{\cdot}$.

The rate constants for the addition of radicals to diazonium cations have been estimated[22] at 0 °C in methanol: $k_5 \approx 10^6$ litre mol^{-1} s^{-1} for $CH_3^{\cdot}$ and $C_2H_5^{\cdot}$ and $k \geq 10^8$ litre mol^{-1} s^{-1} for $(CH_3)_3C^{\cdot}$. This addition is reversible, since high yields of azo-compounds are obtained solely in the presence of relatively high concentrations of metal salts, which reduce the intermediate radical-cation and therby shift the equilibrium towards the final product. According to the authors of two investigations,[21,22] the addition of alkyl radicals to the diazonium cations is significantly accelerated if the degree of charge transfer from the radical to the cation in the transition state of reaction (5) increases. However, this hypothesis conflicts with the acceleration mentioned above, of the addition of isopropyl alcohol β-radicals under the influence of electron-donating substituents in the nucleus of the cation, since evidently the degree of charge transfer from the radical to the cation should fall with increase in the electron-donating capacity of the substituents.

Yet another common and thoroughly investigated type of reactions of radicals with diazonium cations involves electron transfer from the radicals to the cations:

$$R^{\cdot} + ArN_2^+ \rightarrow R^+ + ArN_2^{\cdot} \qquad (6)$$

It has sometimes been suggested (see, for example, Bargon and Seifert[19]) that these reactions proceed in two stages—with the intermediate formation and subsequent decomposition of the radical-cations $Ar{-}N{=}N{-}R^{\cdot+}$.

Evidence for the single-stage course of the reduction of diazonium cations with α-radicals derived from benzyl alcohol has been obtained[15,24] from data on the kinetics of the chain decomposition of diazonium salts initiated by γ-radiation in aqueous solution of the alcohol. Electron transfer from these radicals to the diazonium cations is the rate-limiting chain propagation step in the chain process. It has been found that the $\lg k$ for these reactions are correlated with the σ^+ constants of the substituents in the diazonium cations and that $\rho^+ = 0.55$ (the reaction is accelerated by electron-accepting substituents). We may note that a positive value of ρ has been obtained also for the correlation of the half-wave potentials in the polarographic one-electron reduction of substituted diazonium salts in sulpholan with the σ constants of the substituents in these salts.[25] The above data agree with a single-stage mechanism of electron transfer from the benzyl alcohol α-radicals to the diazonium cations.

The acceleration of the reactions with increase in the electron-accepting capacity of the substituents in diazonium cations has been observed also for the interaction of these cations with the radicals $^{\cdot}CH_2OH$ and $(CH_3)_2^{\cdot}COH$ investigated by pulse radiolysis.[26] The rates of the reactions increase on passing from the primary to the tertiary radical, which agrees with the decrease in the oxidation potential of the radicals[27] and hence corresponds to the mechanism involving electron transfer from the radicals to the cations in the slow stage.

The kinetics and mechanisms of the reduction of diazonium salts by stable triarylverdazyl radicals have been studied.[28] The products of the one-electron oxidation of the radicals, namely the verdazylium cations, were obtained in 90–95% yield. The products of the reduction of the cations ArN_2^+, i.e. the diazenyl radicals $ArN_2^{\cdot}$, were identified with the aid of chemically induced dynamic nuclear polymerisation (CIDNP) of the benzene formed from $PhN_2^{\cdot}$. The choice between the mechanism involving direct electron transfer in the slow stage of the process and the mechanism involving the formation and subsequent homologous decomposition of the radical-cation derived from the azo-compound was made on the basis of kinetic data. The reactions investigated are of first order with respect to each reactant and their rate constants k, calculated from the kinetic curves for the destruction of the radicals and the curves for the accumulation of verdazylium cations, agree over a wide range of variation of k (from 10 to 10^5 mol^{-1} s^{-1}). These data show that, even if the radical-cation is formed in the intermediate stage of the reaction, its stationary concentration is low. The values of $\lg k$ for the reactions considered increase linearly with increase in the reduction potentials of the diazonium cations and with decrease in the oxidation potentials of the verdazyl radicals, which agrees with the mechanism involving direct electron transfer from the radical to the cation in the slow stage. It has also been found that the $\lg k$ for the reactions of the triphenylverdazyl radical with the p-t-butylbenzenediazonium cation in various aprotic solvents decrease with increase in the donor number of the solvent. This is probably associated with the decrease in the equilibrium constant for the formation of the complex, preceding the electron transfer between the reactants, with increase in the strength of the donor–acceptor bonds between the diazonium cation and solvent molecules.

Electron transfer from radicals to diazonium cations has been postulated in the chain propagation stages of many chain processes involving the decomposition of diazonium salts in solutions containing substrates such as alcohols,[3-10,15,20,24,29] ethers [dioxan and tetrahydrofuran (THF)],[13,14,30,31] hypophosphorous acid,[11,12,32-34] cysteine,[34] and 2,4,6-triphenyl-4H-pyran,[35] but the kinetics has been studied in only some of the investigations,[14,15,20,24,30-35] where it was postulated

that the chain propagation process consists in the abstraction of hydrogen atoms from the substrate molecules by aryl radicals or the β-radicals of the substrates and in electron transfer from the substrate radicals formed to the diazonium cations. If the rate of the first of these stages is higher than that of the second, then the rate of the process is limited by electron transfer from the radicals to the cations and chain termination takes place mainly on recombination of the substrate radicals. The increase in the electron-donating capacity of the radicals derived from substrates or in the electron-accepting capacity of diazonium cations can make the first stage rate-limiting and chain termination then occurs on interaction of the aryl radicals or the substrate β-radicals with the diazonium cation.

Since the rate constants for the abstraction of hydrogen atoms from the CH bonds by phenyl radicals are known[36,37] and the rate-limiting chain propagation stage can be found from the type of the overall kinetic equation for the chain process, the above considerations make it possible to estimate the upper or lower limit to the rate constants for reactions (6). Thus, in the hydroquinone-initiated decomposition of diazonium salts in aqueous dioxan, the rate-limiting chain propagation stage involves electron transfer from the dioxan radical to the diazonium cation and the rate constant for this process must be lower than that for the abstraction of the H$^{\cdot}$ atom from the dioxan molecule by the phenyl radical, i.e. lower than the value 4.8×10^6 litre mol^{-1} s^{-1} known from the literature.

We may note that in those cases where the rate-limiting chain propagation stage consists in electron transfer from the substrate radicals to the diazonium cations, a correlation is usually observed between the overall rate of the chain process and the σ constants of the substituents in the nucleus of the diazonium cation with a positive value of the constant ρ (see, for example, Rykova et al.[31]). In doubtful cases, this feature can serve for the confirmation of the nature of the rate-limiting chain propagation stage and for the estimation of the limits of the rate constants for reactions (6).

It has been established[38,39] that the interaction of stable nitroxy-radicals with diazonium salts leads to electron transfer from the radicals to the cations. When crystalline diazonium tetrafluoroborates or chlorides are added to liquid di-t-butyl nitroxide, nitrogen is evolved and immonium salts are formed.[38] The phenyl or *p*-nitrophenyl radicals formed in this reaction recombine with the initial nitroxy-radicals, affording *NN*-di-t-butyl-*O*-phenylhydroxylamine or *NN*-di-t-butyl-*O*-(4-nitrophenyl)hydroxylamine in yields up to 75%, while the 2,4-dinitrophenyl and 2,4,6-tribromophenyl radicals abstract hydrogen atoms from the t-butyl group of the nitroxy-radical, forming *m*-dinitrobenzene or 1,3,5-tribromobenzene in yields of 22 and 13% respectively. The appearance of aryl radicals in the reaction has been confirmed by the formation of substituted bromobenzenes in the presence of CBr_4.

Intramolecular cyclisation leading to fluorescence (the Pschorr reaction) is not observed in the interaction of nitroxy-radicals with diazotised 2-aminobenzophenone, hydrogen atoms being abstracted by the benzophenone radicals from the nitroxy-radicals.[38] However, it was shown later that the interaction of nitroxy-radicals with *o*-substituted diazonium salts in acetone leads to the expected products of the intramolecular cyclisation. These data confirm the radical mechanism of the version of the Pschorr reaction considered.

Electron transfer from radical-anions to diazonium cations is also very common, but its systematic study has begun relatively recently. Reactions of this type have been postulated in chain propagation stages of the decomposition of diazonium salts in alkaline media[7,34] and in aqueous solutions of hypophosphorous acid.[34] It has been assumed[11,12,32,33] that diazonium cations interact with the $H_2PO_4^{\cdot}$ radical in the chain propagation stages of the last reaction; however, it is more likely that the conjugate base of the neutral radical, namely the radical-anion $HPO_2^{\cdot-}$, actually reacts with the cations. This is indicated by the detection of the $HPO_2^{\cdot-}$ species from the characteristic EPR spectrum comprising a doublet (a = 484 G) of doublets (a = 90 G) with a g-factor of 2.0028 in the oxidation of hypophosphorous acid with hydrogen peroxide in the presence of Tl^{3+} ions at pH between 2 and 8, i.e. under conditions where the acid reacts with diazonium salts; under these conditions, the signal of the $H_2PO_2^{\cdot}$ radicals is absent.[40] When a mixture of the salt $PhN_2^+BF_4^-$ and a phenyl radical trapping agent (maleic acid) was added to the given mixture, EPR signals corresponding to $HPO_2^{\cdot-}$ and the adduct of Ph$^{\cdot}$ with maleic acid were identified. It has been suggested[40] that the reaction

$$PhN_2^+BF_4^- + HPO_3^{2-} + H_2O \rightarrow Ph^{\cdot} + N_2 + H_2PO_3^- + HBF_4$$

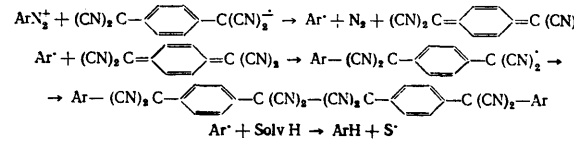
proceeds under these conditions.

The lower limit for the rate constant of the reaction of the diazonium cation with $HPO_2^{\cdot-}$ was found from chain kinetic data for the decomposition of p-$CH_3C_6H_4N_2^+BF_4^-$ initiated by γ-radiation in aqueous H_3PO_2 solution:[34] $k = 2.5 \times 10^6$ litre mol^{-1} s^{-1}. It was also shown in this study that the rate constant for the reaction of the diazonium cation with $HPO_2^{\cdot-}$ is lower than that for the reaction with the radical $^{\cdot}CH_2OH$, i.e. is smaller than 1.8×10^9 litre mol^{-1} s^{-1}.[25]

The rate constants for the interaction of substituted semiquinone radical-cations with substituted diazonium salts in water have been determined[26] by pulse radiolysis. It was found that the introduction of electron-accepting substituents into the aromatic nucleus of the diazonium cations and of electron-donating substituents into the semiquinone radical-anion accelerates the reaction, which agrees with the mechanism involving electron transfer from the radical-anions to the diazonium cations in the slow stage of the process. Comparison of the rate constants for the reactions of diazonium cations with the neutral radicals and radical-anions having identical oxidation potentials showed that the rate depends not only on the redox potential of the radical but also on its charge, since the interaction between ions of opposite charge lowers the activation energy and accelerates the reaction of radical-anions compared with neutral radicals.

The chain propagation stages of the synthetically important radical-chain arylation of quinones by a diazonium salt in aqueous solutions apparently involve the interaction of the diazonium cations with semiquinone radical-anions.[41,42] It has been suggested that complexes of the radical-anions with diazonium cations, having an absorption maximum at 380 nm, are formed in the slow stages of these reactions and then decompose rapidly with evolution of nitrogen. It has been found from overall kinetic data for the arylation process that the rate constant for the formation of the complex is 500 litre mol^{-1} s^{-1}. We may note that the value obtained is doubtful, since it is almost five orders of magnitude lower than the rate constants for the reactions of semiquinone radical-anions with diazonium salts determined by flash photolysis.[43]

The reactions of salts of tetracyanoquinodimethane radical-anions ($TCQD^{\cdot-}$) with the salts p-$XC_6H_4N_2^+BF_4^-$ in acetone or acetonitrile (Solv H) have been used[44,45] to synthesise light-sensitive derivatives of *p*-phenylenedimalonodinitrile:



A detailed study of the influence of the nature of the reactants and of the medium on the rate of reactions of this type has been undertaken.[46] Their kinetics are described by second-order equations—first order with respect to each reactant. The rate of reaction diminishes with decrease in the reduction potentials of the diazonium salts. It increases on passing from $TCQD^{\cdot}$ to the *p*-choranil radical-cation which has a higher oxidation potential than $TCQD^{\cdot}$. The dependence of $\lg k$ for the reactions of $PhN_2^+BF_4^-$ with $TCQD^{\cdot}$, with the *p*-chloronil radical-anion, and with a series of neutral verdazyl radicals in dimethyl sulphoxide on the oxidation potentials of the radicals is described by a single straight line. This indicates a small difference between the contributions of the electrostatic interaction to the free energy of activation by electron transfer from the radical-anions and neutral radicals to the diazonium cation. It has also been established that, in reactions involving electron transfer from radical-anions and neutral radicals to diazonium cations, the selectivity of the reactions diminishes with increase in the reactivity of the radicals. As in the reaction of the diazonium cation with the triphenyl-verdazyl radical, the rate of reaction of the diazonium cation with $TCQD^{\cdot}$ diminishes with increase in the donor number of the aprotic solvent.

The rates of reaction of diazonium salts with the radical-anion salts may be influenced also by the nature of the cation in the latter.[47] Thus in acetonitrile the rate of reaction of $p\text{-}(CH_3)_2NC_6H_4N_2^+BF_4^-$ with the $TCQD^{\cdot}$ radical-anion salts is independent of the nature of the cation M^+ in these salts, while the rates of the reactions in methanol decrease with increase in the ionic radius of M^+. These data have been explained by the fact that in acetonitrile the radical-anion salts exist in the form of solvate-separated ion pairs or free ions, while in methanol the equilibrium between the solvate-separated ion pairs and the less reactive close ion pairs is displaced appreciably towards the latter with increase in the radius of M^+.

The photodecomposition of diazonium salts served as the basis for diazoprinting processes (the production of diazotypes). It has been suggested that in the presence of quinones these reactions involve the interaction of diazonium cations with semiquinone radicals or radical-anions. The kinetics of these processes in aqueous acetonitrile solutions has been investigated.[48] The semiquinone radicals were generated by the interaction of triplet-excited 1,4-benzoquinone with 2,6-di-t-butyl-4-methylphenol. It has been shown that the rates of reaction increase with increase in the electron-accepting capacity of substituents in the aromatic nucleus of the cation and that the pH of the solution, on which depends the ratio of the concentrations of the neutral semiquinone radicals $QH^{\cdot}$ and the radical-anions $Q^{\cdot-}$, formed on acid dissociation of $QH^{\cdot}$, has an appreciable influence on the rate. Thus the rate constants for the reaction of $p\text{-}NO_2.C_6H_4N_2^+BF_4^-$ falls from 2.8×10^8 litre mol^{-1} s^{-1} to 2.9×10^5 litre mol^{-1} s^{-1} as the pH falls from 2.8 to −0.7.

The photochemical reactions of semiquinone radicals of different nature with diazonium salts in heptane, acetonitrile, and a mixture of acetonitrile and water have been investigated.[43] The radical species $QH^{\cdot}$ and $Q^{\cdot-}$ participants in two main processes: disproportionation into Q and QH_2 (or Q and Q^{2-}) and electron transfer to the diazonium ions. The rate constants for electron transfer from the radicals $QH^{\cdot}$ (k_e) and the radical-anions $Q^{\cdot-}$ ($k_{\bar{e}}$) to the salt $p\text{-}ClC_6H_4N_2^+.BF_4^-$ have been determined by flash photolysis. The constants k_e and $k_{\bar{e}}$ increase with decrease in the reduction potentials of the initial quinones Q, which agrees with the mechanism involving electron transfer from the radical to the cation. The values of $k_{\bar{e}}$ are higher than those of k_e by 2–3 orders of magnitude, which indicates a higher reactivity of the radical-anions compared with the neutral radicals. The rate constants for the disproportionation of $QH^{\cdot}$ and $Q^{\cdot-}$ in the media investigated have also been determined. It follows from the data obtained that the electron transfer to diazonium cations with weak electron-accepting substituents can compete in terms of rate with the disproportionation of only the $Q^{\cdot-}$ species present in appreciable concentrations only at high pH of the solution. However, as noted by Becker et al.,[43] in diazoprinting practice the pH of the medium does not exceed 3 and $QH^{\cdot}$ are the main species present in the system. Electron transfer to the diazonium salts containing only highly electron-accepting substituents in the nucleus can compete with the disproportionation of $QH^{\cdot}$.

The photochemical reduction of diazonium salts can proceed via the mechanism involving direct electron transfer to the cation from the sensitiser in an excited state or from the photochemically generated radical in the ground state. In the reactions of diazonium salts with the radicals derived from semiquinones corresponding to thionine or Methylene Blue, it was possible to distinguish these mechanisms. It was found that the direct electron transfer from the sensitiser in the excited triplet state to the cation proceeds with a low efficiency.[49]

The kinetics of the radical-chain photodecomposition of diazonium salts, sensitised by derivatives of anthraquinone or benzoquinone, in aqueous solutions of alcohols, sodium formate, sodium oxalate, and ethylenediaminetetraacetate (EDTA) and in poly(vinyl alcohol) matrices has been investigated.[50–53] The reaction mechanism proposed by the authors had been known previously for the decomposition of salts in alcohols and ethers.[14,15] When an aqueous ethanol is replaced by 0.1 M aqueous solutions of sodium formate, sodium oxalate, and EDTA, the chain length changes and amounts to 500, 4 and 15 respectively instead of 50 in ethanol. When the reaction is carried out in the polymer matrix in the presence of sodium formate, the chain length diminishes to 4. In order to diminish the rigidity of the polymer matrix and to facilitate the development of the dye-sensitised chain photodecomposition reactions of diazonium salts, plasticisers are introduced into the matrix.[54] It has been established that oxygen serves as a trapping agent for radicals and diminishes the chain length.

It has been shown[55] that diazonium cations quench the fluorescence of the triplet-excited anthracene and certain other hydrocarbons via the electron transfer mechanism with formation of hydrocarbon radical-cations in yields close to 100%. A number of other sensitisers in the triplet state transmit energy to the diazonium cations and the excited cations then decompose via a heterolytic mechanism with formation of aryl cations. The homolytic reaction pathway is characteristic only of triplets with a relatively low excitation energy and a high electron-donating capacity.

It has been shown[56] that the biradicals formed on photodissociation of γ-methylvalerophenone can also serve as the initiator of the chain decomposition of diazonium cations in methanol. The chain length in this process is 25. It has been established[57] by EPR that neutral radicals are formed in the photochemical reduction of riboflavin or protonated riboflavin cations in poly(ethylene glycol) films and interact with diazonium cations, initiating the chain process. In aqueous poly(ethylene glycol) solution, the chain length is close to 400, whilst in films it falls to 40. The application of the above initiators makes it possible to shift the region of the spectral sensitivity of diazo-materials to 500 nm.

The photosensitised deocomposition of diazonium salts in micellar solutions has been studied.[58–60] In the case of a surfactant forming negatively charged micelles (sodium dodecasulphonate), dynamic (with $k_d = 8.6 \times 10^{10}$ litre

mol^{-1} s^{-1}) and static (with K_{ass} = 210 mol $litre^{-1}$) quenching of the fluorescence of anthracene by added p-$CH_3C_6H_4N_2^+BF_4^-$ is observed. In the case of a compound giving rise to positively charged micelles (dodecyltrimethylammonium chloride), the efficiency of the dynamic quenching fell (k_q = 1.9 × 10^9 litre mol^{-1} s^{-1}) and static quenching was not observed at all. It was concluded[60] that the efficiency of the quenching is determined mainly by the Coulombic interaction of the charges of the micelle and the quenching agent.

It has been shown[61,62] that the rates of the reactions of ketyl radicals, generated on photoirradiation of α-phenylbenzoin, with p-$ClC_6H_4N_2^+BF_4^-$ increase with increasing fraction of the excited radicals, which is associated with the decrease in the free energy of the electron transfer reactions on excitation.

A study has been devoted to the solution of the problem whether or not the photosensitised decomposition of diazonium salts in the presence of aromatic ketones proceeds via the electron transfer or the energy transfer mechanism.[63] It was demonstrated by the CIDNP method that diazonium salts decompose via the mechanism involving electron transfer from the excited ketones in the T_1 state to the diazonium cations with rate constants of (1.0–9.8) × 10^9 litre mol^{-1} s^{-1}. In the reactions of fluorenone and pyrene with the cations, the electron is transferred from these compounds in the S_1 state, which is most stable.

The data described facilitate the search for diazoprinting compositions incorporating diazonium salts and initiators, which decompose under the influence of light to radicals which interact with the cation initiating their chain decomposition.[64]

Aryl radicals and cations derived from the initial radicals are formed in the reactions involving the reduction of diazonium cations by radicals. These active species can initiate the radical and cationic polymerisation. The use of such systems for photopolymerisation is particularly promising. A system consisting of a photoinitiator (a benzoin ether or potassium oxalatoferrate) and a coinitiator (bisdiazonium salts) has been proposed[65] for the initiation of radical photopolymerisation. It was shown that the bisdiazonium salts induce the photopolymerisation of acrylamide at the same rate as diazonium salts but afford polymers with twice as high a molecular weight. The increase in the molecular weight of polyacrylamide was explained by the fact that in the case of bisdiazonium salts the products of the polymer chain termination contain diazonium groups capable of initiating further polymerisation.

The chain decomposition of diazonium salts can occur on transfer to the latter of an electron from the radical-anions CO_2^- formed on photoirradiation of the complex oxalates $K_3[Fe(Ox)_3]$ and $K_3[Co(Ox)_3]$ at the wavelength of the charge transfer band.[66] The quantum yields in the evolution of nitrogen increase with increasing electron-accepting capacity of the substituents in the diazonium cations. Such systems are effective initiators of the photopolymerisation of acrylamide in the spectral range 400–500 nm.[67] The quantum yield of the photopolymerisation reaches 805 in the case of potassium trisoxalatocobaltate and the p-methoxybenzenediazonium salt.[68]

Systems comprising derivatives of benzoin and diazonium salts have been used to initiate the photopolymerisation of glycidyl isobutyl ether. It was established that the rate of polymerisation increases with increase in the electron-accepting capacity of the substituents in the cation and also in the following series of counterions associated with the p-$ClC_6H_4N_2^+$ cation: $BF_4^- < SbF_6^- < BF_6^-$.[69] Photopolymerising layers for the preparation of relief images in the manufacture of printing plates or recording materials have been proposed on the basis of systems consisting of diazonium salts, oligomers, and photoinitiators (benzoic acid esters[70] or aromatic carbonyl compounds[71]).

It has been established[72] that the reduction of substituted diazonium salts by tetra-t-butylbispyrylium, tetramethyl-p-phenylenediamine ($TMPA^{+\cdot}$), tetraphenylbenzidine, and *N*-methylphenothiazine radical-cations obeys a second-order equation and proceeds via the electron transfer mechanism. The logarithms of the rate constants for these reactions decrease linearly with increase in the standard free energy of electron transfer. The rate of reaction of $PhN_2^+BF_4^-$ with $TMPA^+$ and the selectivity in the reduction of substituted diazonium salts by $TMPA^{+\cdot}$ increase with increase in the electron-donating capacity of the solvent. The addition of crown ethers to the solution accelerates the reaction. The rate increases also with increase in the ionic strength of the solution, Cl^- ions exhibiting a specific accelerating effect. These features of the influence of the medium are the opposite of those in the reactions of organic cations with neutral radicals[28] and with radical-anions.[46] They have been explained[72] by the fact that electron transfer takes place in "bridged" complexes incorporating solvent with crown ether molecules or the Cl^- anion, distributed between the organic cation and the radical-cation. The formation of a "bridge" lowers the electrostatic repulsion between the cation and the radical-cation, brings them closer together, and accelerates the reactions. The magnitude of the effect is determined by the electron-donating capacity and polarisability of the "bridged" molecules. In contrast to this, the reduction of organic cations by neutral radicals or radical-anions requires the desolvation of the reactants and the formation of an ion–dipole complex or a close ion pair in which electron transfer actually takes place.[47]

III. REACTIONS WITH THE ONIUM CATIONS OF GROUP V–VII ELEMENTS

Various thermal and photochemical reduction reactions of iodonium and sulphonium salts as well as the reduction reactions of diazonium salts proceed via a radical-chain pathway. Electron transfer from the chain propagating radical to the onium cations has been postulated in the chain propagation stages of these reactions. It has been shown[73–75] on the basis of kinetic data and observations of CIDNP effects of the products that the reactions of diphenyliodonium chloride with dibutylamine, monoethanolamine, and triethylamine proceed via this mechanism. In the reaction with dibutylamine, the rate-limiting chain propagation stage is electron transfer from the dibutylaminyl radical to the cation. In contrast to this, the rate-limiting chain propagation stage in the interaction of iodonium cations with monoethanolamine and triethylamine is abstraction of hydrogen atoms from the amine by phenyl radicals. The differences between the nature of the rate-limiting stages have been attributed[75] to the fact that the radicals $(C_2H_5)_2N\dot{C}HCH_3$ or $\dot{N}HCH_2CH_2OH$ are less stable than $(C_4H_9)_2N^{\cdot}$; the rate of formation of the first two radicals is therefore reduced, which makes the process rate-limiting.

The interaction of alcohol α-radicals with onium cations has been postulated during the chain propagation stages of the reactions of diaryliodonium cations with 2-nitropropane anions in methanol[76] and also in the reactions involving the decomposition of iodonium[77,78] and sulphonium[79] salts by sodium alkoxides in alcohols. It has been suggested[79] that the reaction with sulphonium cations leads to the formation of radical-cations of the type $R_3S^{+\cdot}$–$C(OH)(CH_3)_2$, but the nature of the

products formed can also be accounted for by electron transfer from the alcohol α-radical to the sulphonium cation.

The kinetics of the reduction of iodonium salts and onium salts of Group VI elements by stable verdazyl radicals and tetracyanoquinodimethane and *p*-chloranil radical-anions has been investigated.[80] It follows from the kinetic data obtained that the diphenyliodonium cation is a much weaker electron acceptor than diazonium ions. However, when the phenyl residue in the iodonium cation is replaced by the perfluoroalkyl residue, the rates of reactions with radicals increase sharply. For iodonium and sulphonium salts, they depend on the inductive effects of the substituents at the central atom and decrease in the following sequence: $n\text{-}C_6F_{13} > n\text{-}C_3F_7 \gg Ph > CH_3$.

The rates of the reactions of the onium cations of Group VI elements with the verdazyl radical in acetonitrile increase with increase in the principal quantum number of the central atom—in the sequence S < Se < Te. The half-wave potentials for the irreversible one-electron polarographic reduction of the cations in acetonitrile increase in the same direction. This finding has been explained by the fact that, in the transition states of the reaction considered, the bond between the central atom and the carbon atom of the substituent is appreciably weakened. The strength of this bond falls with increase in the principal quantum number of the central atom. This lowers the standard free energy and the energy of the reorganisation reactions in the above series and increases the rate.[81] An analogous behaviour has been observed in the series of isotypical onium cations of Group V and VII elements with alkyl and aryl substituents at the central atom. The ease of their irreversible polarographic reduction increases in the following series of cations: ammonium < phosphonium < arsonium,[82] chloronium < bromonium < iodonium.[83] The explanation of this feature is analogous to that quoted above.[81]

Processes in which onium salts undergo one-electron reduction have been used to generate alkyl or aryl radicals. The study of the products of the reduction of sulphonium salts of different structure by graphite or naphthalene radical-anions in tetrahydrofuran led Beak and Sullivan[84] to the following reaction mechanism:

$$RR'R''S^+ \xrightarrow{e^-} RR'R''S^\cdot \rightarrow R^\cdot + R'SR'' .$$

The selectivity of the bond dissociation in the radical $RR'R''S^\cdot$ depends on the nature of the residues R and in the reduction of monophenylsulphonium salts diminishes in the following sequence of R: benzyl > s-alkyl > n-alkyl > methyl > phenyl. It has been suggested that an electron is transferred in the first stage of the reaction from the radical-anion to the phenyl residue of the sulphonium cation and a π-ligand radical-anion associated with the sulphonium cation is formed. This species then decomposes into a sulphide and a hydrocarbon radical, it being assumed that the transition state of the decomposition process involves the overlap of a singly occupied molecular orbital of the aromatic nucleus with the σ* orbital of the homolytically dissociating bond. The selectivity of the decomposition is determined mainly by the relative energies of the radicals formed, although it is also influenced by steric factors. Alkylsulphonium cations are not reduced by the radical-anions employed, since the energy of their highest occupied molecular orbital is much higher than for the phenyl-substituted salts.

Another mechanism of the reduction of sulphonium salts, involving a synchronous electron transfer and the dissociation of the S–R bond, has been proposed.[85] It is based on the observed high sensitivity of the peak potentials on the voltage–current curves for the electrochemical reduction of phenyl- and naphthyl-dialkylsulphonium salts to the electron-accepting capacity of the leading group, which determines the relative energy of the σ* molecular orbital of the bond ruptured on reduction.

The nature of the radicals formed in the electrochemical reduction of sulphonium cations in the presence of radical trapping agents (nitrosodurene, t-butyl phenyl nitrone) has been investigated by the cyclic voltamperometric and coulometric methods at a constant potential with recording of the intermediate products by EPR.[86] In certain cases difficulties arose, associated with the greater ease of the reduction of the trapping agents than of the cations. They were overcome by using the indirect homogeneous reduction of the cations by redox catalysts (anthracene, 1,8-dinitronaphthalene), whose electrochemical reduction occurs at more positive potentials than the reduction of the trapping agents. Under these conditions, the radical-anions formed from the catalysts do not reduce the trapping agent but do reduce the sulphonium cations, being themselves oxidised to the initial hydrocarbons.

A preparative study of the products of the electrochemical reduction of sulphonium and butyltrimethylammonium salts, carried out using electron transferring agents such as fluorene and *p*-cyanoaniline, showed that alkylated derivatives of the transferring agents are formed with a high current yield.[87] In this connection, we may point out that the reactions of onium salts with electrochemically generated radical-anions[88,89] or radical-dianions[90] can serve as a convenient method for the alkylation or arylation of organic compounds formed on oxidation of these radical-anions. The reactions of tetraalkylammonium salts with the electrochemically generated triphenylphosphine or triphenylphosphine oxide radical-anions lead to the exchange of the organic residues linked to the phosphorus:[89]

$$Ph_3P \xrightarrow{e^-} Ph_3P^{\cdot-}$$
$$Ph_3P^{\cdot-} + (C_4H_9)_4N^+ \rightarrow [Ph_3PN(C_4H_9)_4]^\cdot$$
$$[Ph_3PN(C_4H_9)_4] \rightarrow C_4H_9\dot{P}Ph_3 + (C_4H_9)_3N$$
$$C_4H_9\dot{P}Ph_3 \rightarrow Ph^\cdot + C_4H_9PPh_2$$
$$C_4H_9PPh_3 \rightarrow C_4H_9^\cdot + Ph_3P .$$

The possibility of the reactions of electrochemically generated neutral radicals and radical-anions with onium cations, usually employed as supporting electrolytes in electrochemical synthesis in aprotic solvents of low polarity, must be taken into account in the reduction of organic compounds at high cathodic potentials. Thus, in the electrochemical reduction of benzonitrile in a solution of a tetraethylammonium salt, a reaction of the type of Hofmann degradation of the tetraalkylammonium cation by the benzonitrile radical-anion takes place.[91] It has been found that the rate of disappearance of the radical-anion increases linearly with increasing concentration of the ammonium salt.

In reactions with onium cations, the radical-anions can serve either as donors of one electron or as nucleophiles. In order to elucidate the relative contributions of these types of reaction of the benzophenone radical-anion, use was made of the aryltrimethylammonium salts, which give rise to N–Ar bond dissociation products in one-electron reduction and to products of the rupture of the $N-CH_3$ bonds following the attack by nucleophiles.[92,93] It was found that the above ratio is 2:3 for the reaction of $(C_6H_5)_2CO^-K^+$ with $C_6H_5N^+(CH_3)_3ClO_4^-$ in THF.[93] It increases with increase in the electron-accepting capacity of the substituents in the aromatic nucleus of the ammonium cation. When the nature of the counterion in the radical-anion salt is varied, the contribution of the nucleophilic substitution diminishes in the sequence $K^+ > Na^+ > Li^+$. These data[93] led to the conclusion

that the nucleophilic substitution process is more sensitive to the nature of the counterion M^+ in the radical-anion salt than the electron transfer process and that the latter is more sensitive to the structure of the electrophile than nucleophilic substitution.[92]

Yet another type of reaction with ammonium cations is characteristic of radicals having pronounced electrophilic properties (Cl_2^-, HPO_4^-, SO_4^-, $OH^\cdot$), which abstract hydrogen atoms from the alkyl substituents of the cation. The rates of reaction increase with increase in the number of C–H bonds in the alkyl residues and the relative reactivity of the radicals increases in the sequence $Cl_2^- < HPO_4^- < SO_4^- < OH^\cdot$, which is identical with the series based on the relative reactivities of the radicals in processes involving the abstraction of a hydrogen atom from other aliphatic compounds. The data described show that the reactions of radicals with ammonium cations involve the abstraction of $H^\cdot$ atoms in the rate-limiting stage. The influence of the positively charged nitrogen atom is manifested by a decrease in the rate constant for the abstraction of $H^\cdot$ from the α-carbon atom by two orders of magnitude and from the β-carbon atom by a factor of five compared with the rate constant for the abstraction of $H^\cdot$ from aliphatic hydrocarbons.[94]

A series of studies[95–98] have dealt with the influence of added diazonium, iodonium, and sulphonium salts on the yields and molecular weights of the polymers formed in the thermal or photochemical cationic polymerisation of alkyl vinyl ethers or THF. It was found that in the presence of sources of radicals (azobisisobutyronitrile, benzoyl peroxide) but in the absence of onium salts, the thermal polymerisation of these monomers does not occur, as happens also in solutions of the onium salts in the monomers. However, polymerisation does take place when both a radical initiator and an onium salt are added simultaneously to the solution. The following mechanisms of the formation of cations (polymerisation initiators) have been proposed:

$$X^\cdot + CH_2{=}CHOR \rightarrow X{-}CH_2\dot{C}HOR\,,$$
$$\sim\!-CH_2\dot{C}HOR + Ar_2I^+ \rightarrow \sim\!-CH_2CH{=}\overset{+}{O}{-}R + ArI + Ar^\cdot,$$
$$Ar^\cdot + CH_2{=}CHOR \rightarrow ArCH_2\dot{C}HOR\,,$$
$$ArCH_2\dot{C}HOR + Ar_2I^+ \rightarrow ArCH_2,\ CH{=}\overset{+}{O}{-}R + ArI + Ar^\cdot,$$
$$X^\cdot + \langle\!\rangle\!\!\rangle \rightarrow XH + \langle\!\rangle\!\!\rangle^\cdot \xrightarrow{Ar_2I^+} \langle\!\rangle\!\!\rangle^+ + ArI + Ar^\cdot\,.$$

Here $X^\cdot$ is a radical derived from the initiator and $\sim\!-CH_2\dot{C}HOR$ is the macroradical. Evidently the role of the onium cations consists in the one-electron oxidation to carbonium ions of the radicals, formed with participation of the initiators or macroradicals. If these carbonium ions are unstable and decompose with elimination of protons, then the latter can also initiate polymerisation.

The method considered is especially effective in cationic photopolymerisation. Irradiation with hard ultraviolet light is necessary for the initiation in the absence of onium salts and the quantum yields are low, whereas in the presence of onium salts, the radical photoinitiators may be benzoin and its ethers or alkoxyacetophenones, which absorb light at wavelengths greater than 380 nm and decompose with high quantum yields. Detailed reviews[99,100] have been devoted to the development of initiating systems for photopolymerisation processes involving electron transfer to onium cations of different types from sensitisers in the excited state or from nucleophilic radicals formed on photolysis of benzoin derivatives and ketals and also on photoabstraction of hydrogen from aromatic ketones.

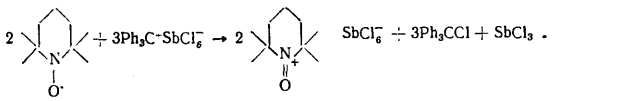
IV. REACTIONS WITH CARBONIUM IONS

The reactions of neutral radicals and radical-ions with carbonium ions have been postulated in the stages of certain radical processes involving carbonium ions, but there have been scarcely any quantitative studies of such processes. Two mechanisms of these reactions have been proposed—the one-electron reduction of the carbonium ion by the radical to the corresponding hydrocarbon radical or the recombination of the reactants.

The reactions in which triphenylcarbenium ions are reduced by a nitroxy-radical give rise to the stable triphenylmethyl radical; in the absence of atmospheric oxygen and water, an equilibrium displaced towards the initial reactants is established in organic solvents:

$$\rangle N{-}O^\cdot + Ph_3C^+ClO_4^- \rightleftarrows \rangle\overset{+}{N}{=}OClO_4^- + Ph_3C^\cdot\,.$$

In the presence of oxygen, which binds triphenylmethyl radicals, this equilibrium is wholly displaced to the right and triphenylmethyl peroxide, triphenylmethanol, and an immonium salt are formed. If $SbCl_6^-$ is the anion in the salt, then the anion and not the carbonium ion is reduced:[101]



In the reaction of $Ph_3C^+ClO_4^-$ with di-t-butyl nitroxide in the presence of oxygen, the peroxy-radical $Ph_3CO_2^\cdot$ has been shown[102] to abstract a hydrogen atom from the alkyl group of the nitroxide with formation of the hydroperoxide Ph_3CO_2H, the olefin $H_2C{=}C(CH_3)_2$, and the nitroso-compound $(CH_3)_3.CN{=}O$.

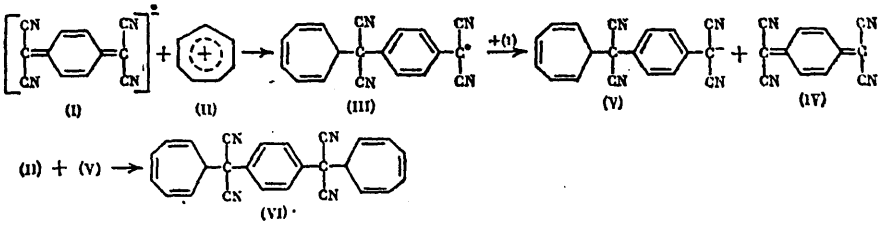
The formation of bitropyl in the reduction reactions of the tropylium cation may be the result of the recombination of tropyl radicals or of the attack by the tropyl radical on the tropylium cation and the subsequent reduction of the bitropyl radical-cation to a neutral compound. The latter mechanism has been proposed for the electrochemical reduction of tropylium (Tp^+) fluoroborate in acetonitrile, which leads to bitropyl:[103]

$$Tp^+ + e^- \rightarrow Tp^\cdot\,,$$
$$Tp^+ + Tp^\cdot \rightarrow Tp_2^{\cdot+}\,,$$
$$Tp_2^{\cdot+} + Tp^\cdot \rightarrow Tp_2 + Tp^+\,.$$

This mechanism is based on the agreement between the observed experimental slope of the polarographic reduction wave and the calculated slope for the mechanism quoted.

The reaction of tropylium fluoroborate with the oxygen radical-anion leads to benzene, benzaldehyde, cycloheptatriene, CO, and O_2.[104] It has been suggested that O_2^- recombines with the cation in the first reaction stage. This is based on the ratio of the products of the reaction of the tropylium salt with a typical nucleophile—the O_2^{2-} anion, which does not differ from the ratio of the products of the reactions of the salts with O_2^-.

The interaction of the lithium salt of the tetracyanoquinodimethane radical-anion (I) with tropylium iodide (II) in acetonitrile affords tetracyanoquinodimethane (IV) and αααα′-tetracyano-αα-ditropyl-p-xylene (VI). The following reaction mechanism has been proposed on the basis of the high yields of these products and the absence of bitropyl among them:[105]



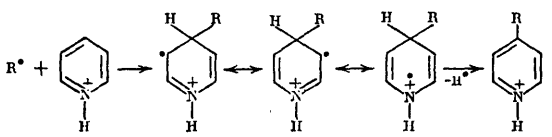
Here the radical-anion plays the role of the nucleophile. However, the product (IV) can also be formed as a result of the one-electron reduction of the cation (II) by the radical-anion (I). The reaction of compound (IV) with the tropyl radical (VII) formed simultaneously gives rise to the product (VI) if the rate of reaction of the species (IV) with (VII) is higher than the rate of dimerisation of the radicals (VII).

A mechanism of the last type, involving electron transfer from the radicals to the tropylium cation, has been proposed on the basis of kinetic data and the analysis of the products of the reactions of tropylium fluoroborate with substituted verdazyl radicals and tetracyanoquinodimethane or *p*-chloranil radical-anions.[106] It has been confirmed by the finding that the rates of these reactions increase with decrease in the oxidation potentials of the radicals and by the fact that the linear relation between the logarithms of the rate constants and the half-wave potentials for the polarographic reduction of the cations, which is characteristic of electron transfer reactions, has been observed for the reactions of the verdazyl radical with substituted diazonium, tropylium, and 2,4,6-triphenylpyrylium salts in acetonitrile.

In contrast to the reactions of diazonium cations with the triphenylverdazyl radical and with the tetracyanoquinodimethane radical-anion, whose rate diminishes with increase in the donor number of aprotic solvents,[28,46] the rate of reduction of the tropylium cation by the triphenylverdazyl radical depends only slightly on this parameter of the medium. This difference has been explained[106] by the fact that the increase in the degree of delocalisation of the charge on passing from the diazonium to the tropylium cation entails a decrease in the energy of the specific solvation of the tropylium cation by electron-donating solvents. As a consequence of the low specific solvation energy, the rates of the reactions of the tropylium cation with the radicals depend significantly on the non-specific solvation of the cation and the radical, so that $\lg k$ increases with increase in $1/\varepsilon$ (where ε is the dielectric constant of the medium). The rate of reaction of the tropylium cation with the tetracyanoquinodimethane radical-anion diminishes with increase in the polarisability of the solvent P, since an increase in P promotes the solvation of the readily polarisable radical-anion.

V. REACTIONS WITH THE CATIONS OF HETEROAROMATIC COMPOUNDS

The interaction of nucleophilic radicals with protonated heteroaromatic bases leads to homolytic substitution products, for example:



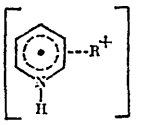
In recent years, reactions of this type have acquired synthetic importance.[107-111] Their rates are high and they exhibit a high positional selectivity and selectivity with respect to the substrate, in contrast to radical substitution reactions involving the molecules of neutral aromatic compounds, which are characterised by relatively low rates and positional selectivity and also by a weak sensitivity of the rate to the nature of the substituents in the aromatic nucleus. It has been suggested[112,113] that the principal cause of the above differences is appreciable polar effects in the reactions of the radicals with the cations. The transition state in these reactions is a charge-transfer complex and the degree of charge transfer is determined by the electron-donating capacity of the radical (the energy level of its singly occupied molecular orbital) and by the electron-accepting properties of the cations (the level of their lowest unoccupied molecular orbital).

The view described above has been confirmed by a number of observations. Thus the rates of the reactions of the heptyl radical with substituted pyridinium cations increase with increase in the electron-accepting capacity of the ring substituents, which is associated with a decrease in the activation energy for a constant pre-exponential factor. The activation energy falls and the rate and selectivity increase, because electron-accepting substituents stabilise the transition state corresponding to the electron transfer.[112]

It has been found[113] that the relative rates of homolytic substitution in the α-position in the rings of γ-substituted pyridines in an acid medium diminish with increase in the ionisation potential of the radicals (on passing from the benzyl to the phenyl radical) and also with increase in the σ constants of the substituents in the rings of the benzyl radicals.

We may note that the rule governing the correlation between the reactivity and selectivity, according to which an increase in the rates of reactions entails a decrease in their selectivity, breaks down in the cases considered. It has been suggested[112] that this rule does not hold at all in radical reactions with a highly polar transition state. However, it follows from certain data[26,46] that this rule does hold in reactions involving total electron transfer from radicals to diazonium cations.

The influence of the nature of the solvent on the kinetics of the reactions considered has been studied in relation to the bioxanyl, benzoyl, carbamoyl, α-aminomethyl, and undecyl radicals with protonated 4-cyano- and 4-methyl-quinolines.[114] An increase in the content of water in dioxan and also in the concentration of acetic acid in dioxan or in dimethylformamide increase the reaction selectivity. This has been explained by the interaction of water or acid molecules with the unshared electron pairs of the radicals, which increases the ionisation potential of the latter and diminishes the contribution by the form

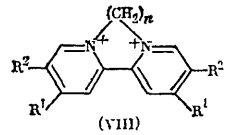


to the transition state. The reaction is thereby slowed down and its selectivity increases. We may note that this explanation does not take into account the change in the solvation of the cations and furthermore contradicts the increase in selectivity with increasing rates of the reactions considered discovered by Citterio et al.[112]

The limiting case of a polar transition state is observed in processes involving total electron transfer from the radical to the cation of the heteroaromatic compound. In such cases, electron transfer products are formed instead of the products of the addition of the radicals to the cations. Total electron transfer may be expected in the reactions of cations with nucleophilic radicals such as $(CH_3)_2\dot{C}OH$, $(C_6H_5)_2\dot{C}OH$, and $C_{10}H_8^{\cdot-}$. The study of the kinetics of the interaction of the radicals $(CH_3)_2\dot{C}OH$ with substituted pyridinium cations in water revealed a correlation between $\lg k$ and the σ constants of the substituents in the cation with the very high positive value $\rho = +8.5$.[115] This observation is a serious argument in support of a transition state close to a charge-transfer complex.

The formation of radicals from the cations of heteroaromatic compounds on their reduction by the photochemically generated radicals $(C_6H_5)_2\dot{C}OH$ or $C_{10}H_8^{\cdot-}$ has been demonstrated unambiguously by EPR.[116] The interaction of cations with classical ionic nucleophiles (OH^-, tertiary amines) leads to the same heteroaromatic radicals. It has been suggested[16] that in all the cases quoted an electron is transferred from the nuclophile to the electron-accepting cation.

The kinetics and the equilibrium in the reduction of dications having the general formula



(VIII)

where $n = 2-4$, $R^1 = H$ or CH_3, and $R^2 = H$ or CH_3, in their interaction with e_{aq}, $CO_2^{\cdot-}$, and $(CH_3)_2\dot{C}OH$ in water have been investigated by pulse radiolysis[117] and it has been found that the rates of the reactions with equated electrons are independent of the reduction potentials of the dications, while the rate of electron transfer from the radicals falls with decrease in these potentials. The rate constants for electron exchange between the radical $(CH_3)_2\dot{C}OH$ and protonated acetone and between the substituted pyrazinium bromide radical-cation and its unreduced form have been estimated from data derived from the equations of the theory of outer-sphere electron transfer reactions developed by Marcus. They proved to be $(2-6) \times 10^6$ litre mol^{-1} s^{-1} and 5×10^7 litre mol^{-1} s^{-1} respectively.

Irradiation of solutions of benzophenone or xanthone and *NN'*-dimethyldipyridinium dichloride (MB^{2+}) in aqueous isopropyl alcohol solution by light at a wavelength greater than 366 nm leads to the generation of the radical-cations $MB^{\cdot+}$ as a result of electron transfer to MB^{2+} from the photochemically generated ketyl radicals or from the alcohol α-radicals. The radical-cations reduce water with evolution of hydrogen, being reoxidised at the same time to the initial dications.[118,119] A significant increase in the quantum yield in the decomposition of water has been achieved by irradiating solutions of γ-ketoalcohols and MB^{2+} in aqueous acetonitrile solution by near ultraviolet light.[120] Thus the radicals $PhC(OH)CH_2$. $CH_2C(OH)Ph$, which reduce MB^{2+} to $MB^{\cdot+}$ with a high rate constant [$(1-3) \times 10^8$ litre mol^{-1} s^{-1}] and a quantum yield of 0.7, have been generated in the system with $PhCH(OH)CH_2$. $.CH_2COPh$.

The formation of the radical dimers in the electrochemical reduction of 3-ethyl-2-methylbenzothiazolium (BT^+) as well as the formation of bitropyl in the reduction of tropylium cations are treated as a result of the attack by the electrochemically generated radical on the initial cation:[121]

$$BT^+ \xrightarrow{e^-} BT^{\cdot},$$
$$BT^+ + BT^{\cdot} \rightarrow BT\text{-}BT^{\cdot+},$$
$$BT\text{-}BT^{\cdot+} \xrightarrow{e} BT\text{-}BT,$$
$$BT\text{-}BT^{\cdot+} + BT^{\cdot} \rightarrow BT\text{-}BT + BT^+.$$

The voltamperogram of the cation has two peaks. The first corresponds to a reversible process at a high rate of scanning of the potential, while the second peak corresponds to an irreversible process at all the rates of scanning of the potential investigated. The mechanism presented above was proposed on the basis of the dependence of the heights and potentials of both reduction waves for the cation on its concentration.

VI. CONCLUSION

In this Section we shall deal with certain general questions of the kinetics and mechanisms of the reactions considered. The data examined in the review show that the main types of reactions of organic cations with radicals involve the addition of the latter to the cations and electron transfer between these reactants. The reactions in which a hydrogen atom is abstracted from the C–H bonds of the hydrocarbon substituent of the cations are encountered much more rarely. They are characteristic of electrophilic radicals, for example, of $OH^{\cdot}$ and $SO_4^{\cdot-}$.

The presence of a charge on organic cations and the low energy of their lowest unoccupied molecular orbitals may be noted as characteristic features of the electronic structure of such species. The high electron affinities[122] and half-wave potentials for polarographic reduction[123] are related to these features. Since the majority of the radicals considered in this review are nucleophilic in character, one can assume that the main factors determining the direction and energetics of both addition and electron transfer reactions between radicals and cations are the Coulombic interaction between these species and the interaction of the singly occupied molecular orbital of the radicals, which have a high energy, with the lowest unoccupied orbital of the organic cations. The attack by the radicals should therefore be directed to the atoms of the cation having the minimum electron density. These conclusions are confirmed by data obtained for the recombination of cations of the type $H-\overset{+}{C}=O$ and $HO-\overset{+}{C}=O$, etc. with hydrogen atoms in the gas phase:[124] the activation energy for the addition of the $H^{\cdot}$ atom to the heteroatom is considerable, while the activation energy for the addition to carbon is low or zero.

The polar character of the transition state in the addition of electron transfer reactions considered is usually reflected by high positive values of the constants ρ in correlation equations linking the logarithms of the rate constants with the σ constants of the substituents in the aromatic nuclei of the cations[15,24,31,35,69,112,115] and the α constants in the equations relating the free energies of activation for the reactions to the free energies of electron transfer between the reactants.[125] The polar character of the transition state is also manifested by the acceleration of the reactions with increase in the electron-accepting capacity of the substituents in the cation[15,24,26,28,43,46,69,72,80,112,115] and in the electron-donating capacity of the radicals.[22,26,28,46,48,72,80,106,113,117] However, we may note that a negative value of ρ has been

obtained for the addition of isopropyl alcohol β-radicals to diazonium cations according to kinetic data for the chain radiolysis of diazonium salts in aqueous isopropyl alcohol.[15] This observation needs to be checked by a direct kinetic method.

A distinctive feature of the reactions involving the addition of radicals to cations investigated hitherto is the increase in selectivity with increase in the reactivity of the radicals or the cations,[112] while in the reactions involving electron transfer from the radicals to the cations the usual rule operates—the selectivity diminishes with increase in reactivity. The reactions involving the reduction of onium cations of Group VI elements by radicals are now known to be an exception to this rule.[81]

The rates of the reactions considered depend not only on the electron-donating capacity of the radicals and the electron-accepting capacity of the cations but also on the sign and magnitude of the charges on the radicals. For the reactions of neutral radicals with cations, the contribution of the ion–dipole interaction to the free energy of activation may be neglected, while for the interaction of radical-ions with cations this contribution is significant; for example, in acetic acid, for a distance between the reactants in the collision complex of 5 Å, this contribution is more than 40 kJ litre mol^{-1}.[126] In the reactions between radical-ions and large cations in media with a high dielectric constant, this contribution is reduced and in slow reactions is insignificant.[46] It increases, for example, with increase in the electron-donating capacity of radicals, leading to a sharp acceleration of the reactions.[26]

In contrast to the reactions involving electron transfer from the radicals to neutral organic compounds, in which the effects of the medium are determined by the solvation of the polar transition state,[127] in reactions involving electron transfer from the radical to the cations these effects are associated mainly with the solvation of the initial reactants. It has been shown for the reactions with electron transfer from neutral radicals, radical-anions, and radical-cations to the diazonium and tropylium cations[72,103] that the character of the influence of the nature of the solvents, of the added crown ethers, and of the nature of the counterions depends on the characteristic features of the structure of the organic cations and the charge on the radicals.

The kinetics of the reduction of organic cations by radicals can be described in terms of the theory of the outer-sphere electron transfer reactions developed by Marcus.[128] The rate constants k for more than 90 reduction reactions of diazonium, tropylium, verdazylium, and pyrylium cations with neutral radicals, radical-anions, and radical-cations as well as with diamagnetic organic molecules have been found[125] from the redox potentials of the reactants with the aid of the equations of this theory. It has been shown that, when account is taken of the energy of the reorganisation of only the outer coordination sphere, the calculated constants k exceed the experimental values by 1–7 orders of magnitude. Quantum-chemical calculations have shown that the reduction of the diazonium and tropylium cations to the corresponding radicals is accompanied by a significant change in structure, which leads to high energies of reorganisation of the inner coordination sphere of the cations in the reduction process. Calculation of the constants k taking this factor into account yielded a satisfactory agreement between the experimental and calculated values within the limits of 1–2 orders of magnitude.

It has been shown[125] that processes involving direct electron transfer to organic cations can be distinguished from processes in which electron transfer is preceded by the formation of an intermediate product of the recombination of the reactants with the aid of calculations based on the equations of the Marcus theory. Only for reactions of the first type is it possible to obtain a satisfactory agreement between the experimental constants k and the values calculated from the redox potentials of the reactants and the energies of the reorganisation reactions. For reactions of the second type, the experimental recombination rate constants exceed by many orders of magnitude the values calculated from the Marcus theory. This difference is greater the stronger the bond in the intermediate compound ruptured on dissociation into the electron transfer products.

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