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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Role of Triplet States of Aryldiazonium Cations in the Meerwein Reaction

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Abstract—The mechanism of the Meerwein reaction was interpreted on the basis of quantum-chemical calculations of the optimal geometry, electronic spectra, and ground state of a large number of diazonium cations. The relationship of this process with the triplet excited state of aryldiazonium cations and the role of spin catalysis in thermal excitation of these states via ligand-to-metal and metal-to-ligand electron transfer involving organic ligands and complex copper chlorides as catalysts were examined.

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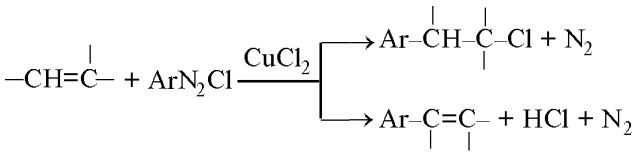
Meerwein reaction with all its modifications, allowing wide variation of the spectrum of the products obtained, is widely used in modern fine organic synthesis. The Meerwein reaction is the reaction of unsaturated compounds with aryldiazonium salts in the presence of copper(II) chloride as catalyst [1]:



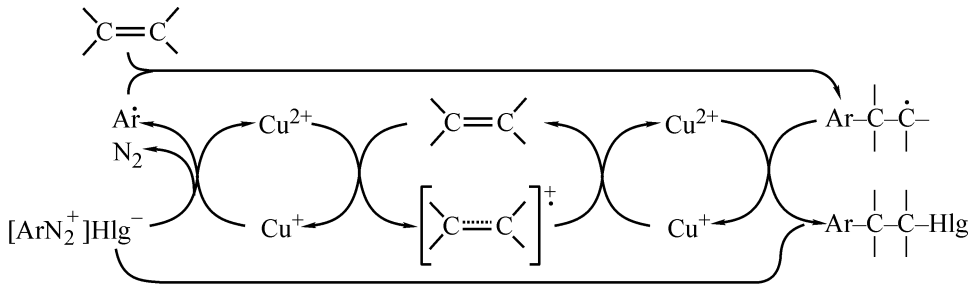
High preparative value of this reaction calls for its experimental and theoretical study. Understanding of the mechanism of this reaction and of the role of its intermediates and of reaction conditions is very important, as it will make the synthesis more efficient.

Based on generalization of a large volume of experimental data, Obushak et al. suggested a radical-ion mechanism of the Meerwein reaction [2]. The catalyst, actually occurring in the reaction mixture in the form of the Cu^{2+}/Cu^{+} couple, is considered as electron-transfer agent, i.e., as a redox agent. Within the framework of this mechanism, the diazo cation reduced with Cu^{+} ions to the radical eliminates a nitrogen molecule, transforming into an aryl radical. The Cu^{+} ions are generated in the reaction mixture by oxidation with Cu^{2+} ions of substrate molecules, always present in a certain excess, to radical cation.

Aryl radical reacts with another substrate molecule, transforming into an alkylaromatic radical. The resulting radical is oxidized with Cu^{2+} to the cation, which binds the halide ion to give the final product. The reduced form of the catalyst transfers electron to the radical cation to form the Cu^{2+} cation, with closure of the catalytic cycle (Scheme 1).

The olefin radical cation not only acts as a connecting

Scheme 1.



link between the oxidized and reduced forms of the catalyst, but is also a criterion for the reaction occurrence [3]. As will be shown below, quantum-chemical calculations show that the nitrogen molecule cannot be eliminated from the diazenyl radical formed by reduction of the diazo cation in the ground singlet state, which is a serious drawback of the suggested scheme. Our quantum-chemical calculations led us to an alternative idea of the role of Cu^{2+} in the initial step of the Meerwein reaction.

The optimal geometry of aryldiazonium cations was calculated by the AMBER molecular mechanics method [4], after which optimization and electronic structure calculation were performed by the Hartree–Fock self-consistent field method in the PM3 semiempirical version [5].

The electronic spectra of diazo cations were calculated by the configuration interaction (CI) method [6] for single excitations. To form the active CI space, we used an orbital criterion: five occupied and seven unoccupied MOs of the required symmetry, forming a recurring set of active orbitals at all internuclear distances along the reaction coordinate, were included in CI calculations.

The ground state of the cations was calculated using the restricted Hartree–Fock (RHF) formalism. The optimized structures of triplet excited states were calculated by the unrestricted Hartree–Fock (UHF) method [7] and by CI method along the reaction coordinate.

By these methods we calculated a large number of aryldiazonium cations with *o*-, *m*-, and *p*-substituents of both donor and acceptor type [8], with analysis of the IR and Raman spectra of these substances. In this study we consider the reaction of phenyldiazonium activation, although, according to the preliminary data, the results we obtained are more general.

Calculations of molecular orbitals of phenyldiazonium cation in the ground singlet state show that the lowest unoccupied molecular orbital (LUMO) is bonding along the C–N bond (Fig. 1). This fact indicates that reduction of the diazo cation to radical should strengthen the C–N bond. This interesting fact suggests the idea of the role of excited states of aryldiazonium cations in nitrogen elimination. Мьller et al. [9] demonstrated the possibility of using diazo salts stable in the solid state as photoinitiators of cationic polymerization. The ESR spectra recorded by Мьller et al. [9] confirm the formation of triplet states of intermediates in the course of the photochemical reaction. Here we suggest the possibility of triplet excitations in the dark reaction also. The triplet excited states can be formed owing to the catalytic activity of Cu^{2+}, following the concept of spin catalysis applied previously to hydrogenation and dehydrogenation reactions [10–15].

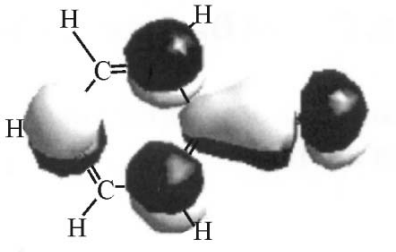


Fig. 1. Lowest unoccupied molecular orbital of phenyldiazonium cation.

The spin catalysis concept consists in that a chemical reaction is accelerated by exchange and magnetic interactions caused by spin rearrangement involving a homogeneous or heterogeneous catalyst. Thus, the catalytic activity of Cu^{2+} can be accounted for in terms of the principle of ligand-to-metal and metal-to-ligand electron donation in interaction of an organic ligand with a transition metal, suggested by Dewar, Duncanson, and Chatt [16, 17].

It is known that the diazo cation has a closed electronic shell (the spin multiplicity is 1), whereas the Cu^{2+} cation has one unpaired electron (spin multiplicity 2). In dilute aqueous medium, the Cu^{2+} ions are in the form of light blue aqua cations $[Cu(H_2O)_6]^{2+}$ having an octahedral structure. Chloride ions displace water molecules from the inner coordination sphere up to the formation of the yellow-green tetrahedral complex $[CuCl_4]^{2-}$. In the process, according to the crystal field theory, the *d* sublevel is split, and the unpaired electron in the $3d^9 4s^0$ configuration is localized on the d_{xz} orbital.

The Cu^+ ions formed in the reaction medium (Scheme 1) will also be fully coordinated in the complex $[CuCl_2]^-$, as they occur in a solution containing excess chloride ions.

The classical Meerwein reaction is performed in aqueous acetone. Acetone acts not only as solvent for olefins insoluble in water, but also as reductant for copper(II) [18]:

$$2CuCl_2 + H_3C{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3 \xrightarrow[-HCl]{} Cl{-}CH_2{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3 + 2CuCl.$$

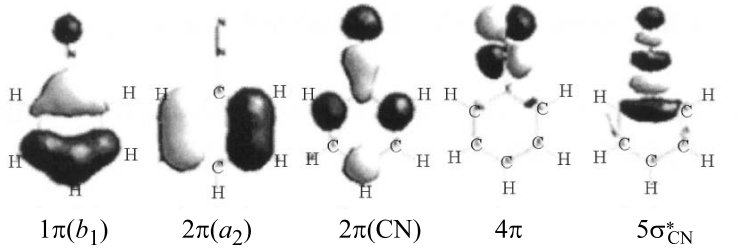


Fig. 2. Some molecular orbitals of phenyldiazonium cation.

Then the reduced form of the catalyst forms a double salt with aryldiazonium chloride and participates in the subsequent transformations [19]:

$$ArN_2^+Cl^- + CuCl \rightleftharpoons ArN_2^+CuCl_2^-.$$

At the same time, Grishchuk et al. [20] emphasize that, in the case of high solubility of olefin in water, the Meerwein reaction can be successfully performed without acetone. In view of this fact, it is unclear how CuCl is formed in an acetone-free medium.

We believe that the reduction of Cu(II) is possible only on cleavage of the multiple bond of the olefin with the formation of a radical cation, as shown in [2]. Acetone acts merely as substrate solvent, which explains why active nitrogen evolution, indicative of the reaction occurrence, starts only on adding olefin [20] which directly participates in the redox catalytic cycle (Scheme 1).

Figure 2 shows the molecular orbitals of the phenyldiazonium cation. Analysis of their dynamics is important for understanding the mechanism of nitrogen elimination.

Molecular orbitals 1 and 2 in the ground state are occupied quasidegenerate orbitals of the phenyl ring. Molecular orbitals 3–5 are unoccupied in the ground state, with π_{CN} being the lowest unoccupied molecular orbital. The behavior of the energy levels of these orbitals in the course of cleavage of the C–N bond is essentially different.

To determine the character of energy distribution of molecular orbitals of phenyldiazonium cation in the ground singlet state, we calculated the correlation diagram as a function of the C–N bond length (Fig. 3).

Figure 3 shows that the energy of the molecular orbital π_{CN} increases with elongation of the C–N bond. At the same time, the energy of the $5\sigma^*_{CN}$ MO monotonically decreases. The curves of the energies of these two orbitals intersect at the C–N bond length close to 1.6 Å. The occupied MOs $\pi(b_1)$ and $\pi(a_2)$ in this point pass through a maximum. All these facts suggest a key significance of this point on the reaction coordinate of the C–N bond cleavage, when $5\sigma^*_{CN}$ orbital becomes the lowest unoccupied molecular orbital.

Analysis of the electronic spectra calculated by the CI method with step-by-step extension of the C–N bond (Fig. 4) confirms that the transitions 5T $\pi(b_1) \rightarrow \pi_{CN}$ and 6T $\pi(a_2) \rightarrow \pi_{CN}$ lead to destabilization of the system, and the excited triplet states arising from the transitions 1T $\pi(b_1) \rightarrow \sigma^*_{CN}$ and 2T $\pi(a_2) \rightarrow \sigma^*_{CN}$ strongly decrease in energy. The 1T transition has a broad energy minimum in the range 1.6–2.0 Å. When getting into this state, the cation undergoes vibrations of large amplitude.

At the same time, the stationary geometry of aryldiazonium triplets strongly depends on the substituent in the aromatic ring. Effective π-electron donors (NH_2, OH, OCH_3) lead to decomposition of the cation in the course of optimization: The C–N bond length becomes close to

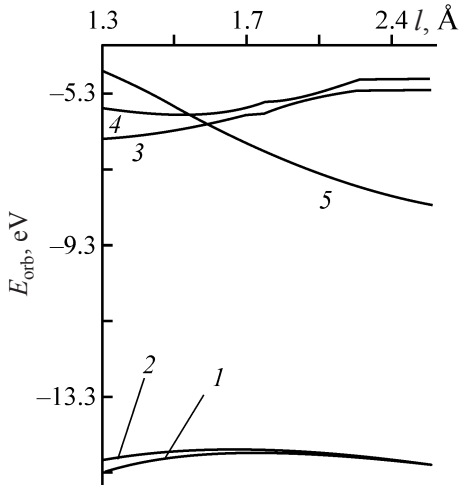


Fig. 3. Energy E_{orb} of molecular orbitals of phenyldiazonium cation as a function of the C–N bond length l in the ground singlet state. (1) $\pi(b_1)$, (2) $\pi(a_2)$, (3) π_{CN}, (4) π', and (5) σ^*_{CN}.

1.8 Å, i.e., the bond is practically broken. With substituents of the first kind, exhibiting weak strength (CH_3, Cl, Br, and also H), in the course of geometry optimization the structure can fall into two minima depending on the starting geometry. One of the minima is at the C–N bond length close to 1.45 Å, whereas the C–N bond length for the other minimum is about 1.8 Å, which also leads to decomposition of the cation. The geometry of the phenyldiazonium cation in the triplet state at a C–N bond length of 1.54 Å becomes nonplanar. The nitrogen atom bonded to the ring deviates from the cation plane by an angle of 28°, whereas the terminal atom remains essentially in the ring plane. Finally, strong electron-withdrawing substituents in the aromatic ring (NO_2, SO_3H) lead only to a nonplanar geometry with the C–N bond length close to 1.45 Å, which corresponds to the quinoid structure of the triplet excited phenyl ring. Thus, although full optimization of the triplet energy gives a more complex reaction coordinate, it is qualitatively consistent with the chosen decomposition model.

Similar results were also obtained by Tsuda and Oikawa [21] who performed CI calculations of phenyldiazonium by the INDO/S method taking into account both elongation of the C–N bond and change in the angle between the ring and CNN group (θ_{CNN}) which remained linear. In this calculation version, the optimal reaction pathway was that involving nitrogen elimination with simultaneous change in the θ_{CNN} angle and elongation of the C–N bond. In this case, the angle θ_{CNN} may reach 80°, which is hardly realistic. Optimization of the triplet geometry shows that the C–N–N fragment in this state is also subject to deformations. According to CI calculations, for getting into the triplet state thermal vibrations of atoms in the cation are sufficient, which is quite understandable physically.

Optimization of the triplet states shows that, at a C–N bond length close to 1.6 Å, there is a small energy barrier.

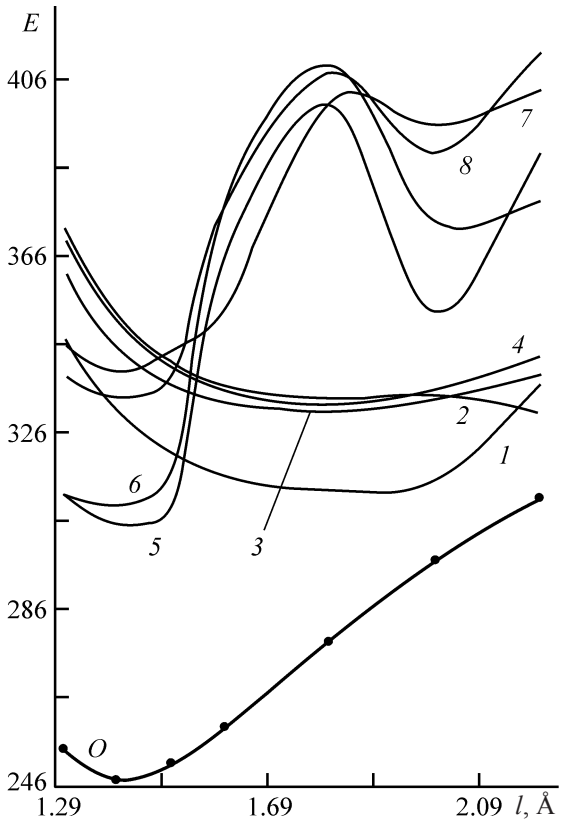
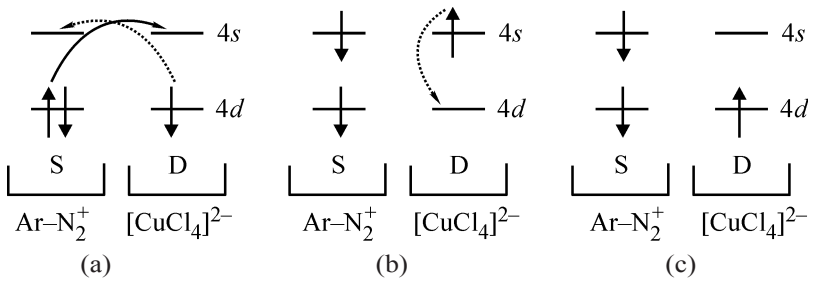


Fig. 4. Energies E of the (0) ground and (1–8) excited states of phenyldiazonium cation at various C–N internuclear distances l. (*1*) T $\pi(b_1) \rightarrow \sigma^*_{CN}$, (*2*) T $\pi(a_a) \rightarrow \sigma^*_{CN}$, (*3*) S $\pi(b_1) \rightarrow \sigma^*_{CN}$, (*4*) S $\pi(a_2) \rightarrow \sigma^*_{CN}$, (*5*) T $\pi(b_1) \rightarrow \pi_{CN}$, (*6*) T $\pi(a_2) \rightarrow \pi_{CN}$, (*7*) S $\pi(b_1) \rightarrow \pi_{CN}$, and (*8*) S $\pi(a_2) \rightarrow \pi_{CN}$.

On its overcoming, the system comes to a broad minimum (Fig. 4). In this triplet state, the highest single-occupied MO is σ^*_{CN}. In going to the triplet state, i.e., upon electron transition to this MO, the system will decompose with the elimination of nitrogen.

It should be emphasized that only the triplet states are important. Singlet excitations have very high energy and therefore should not be taken into account (Fig. 4). The behavior of unoccupied MOs confirms the previously

Scheme 2.



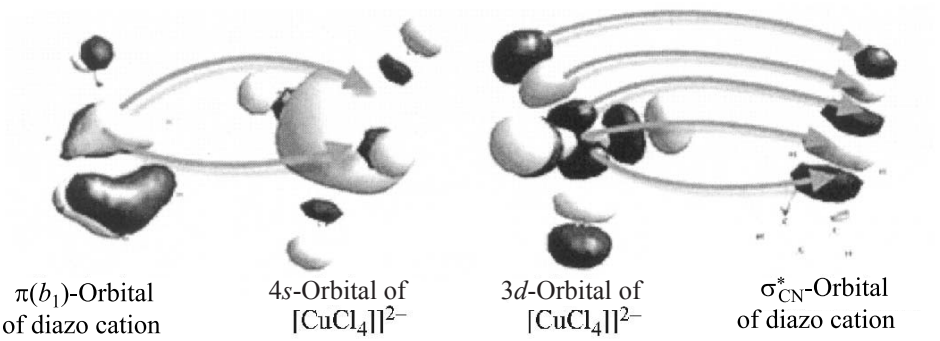


Fig. 5. Correspondence between the orbitals of the catalyst and diazo cation.

suggested spin catalysis mechanism. The role of Cu^{2+} ions having an unpaired electron just consists in providing the transition of the aryldiazonium cation into a triplet due to exchange mechanism of spin catalysis, taking into account the Dewar–Duncanson–Chatt model of ligand-to-metal and metal-to-ligand electron donation (Fig. 2).

The spin catalysis mechanism explains the reaction as follows. An electron from HOMO of the diazo cation passes to the 4*s* orbital of $[CuCl_4]^{2-}$ (ligand-to-metal donation). Simultaneously, an electron from the 3*d* AO of $[CuCl_4]^{2-}$ passes to σ^*_{CN} of the diazo cation to form a triplet state (metal-to-ligand donation). Unpaired electron of the 4*s* orbital of $[CuCl_4]^{2-}$ spontaneously passes to the 3*d* orbital to form the initially doublet state of the catalyst (Scheme 2).

The electron relaxation from the 4*s* to 3*d* AO of the catalyst is caused by the tendency to complete the $(n-1)d$ shell of copper (Scheme 2c). As seen from Scheme 2, for each state (a, b, c) the total spin is 0.5.

The above-described mechanism of the electron transfer is possible owing to interaction of structurally similar orbitals of the catalyst with those of the diazo cation, which makes possible their overlap and, correspondingly, the electron transfer (Fig. 5).

The key role of the solution containing additional Cl^- ions in catalyst activation should be noted. Formation of the complex $[CuCl_4]^{2-}$ leads to the formation of the orbital structure that fits, like a key to a lock, the σ^*_{CN} orbital of the diazo cation and makes possible the mechanism of the ligand-to-metal and metal-to-ligand electron donation (Fig. 5).

The following experimental fact also counts in favor of the key role of $[CuCl_4]^{2-}$: The reaction virtually does not start in the absence of water [19]. It is known that formation of $[CuCl_4]^{2-}$ (and hence of the triplet state of the diazo cation) in an anhydrous medium is impossible.

Thus, interaction of the diazo cation with the catalyst leads to the electron transition to the molecular orbital σ^*_{CN}, which is essentially antibonding with respect to the C–N bond, making possible the elimination of the nitrogen molecule.

Interpretation of the mechanism of nitrogen elimination in the Meerwein reaction from the viewpoint of the spin catalysis theory is also reflected in the Kalnin'sh concept of thermal electronic excitation [22]. The main idea of this concept is that the course of thermochemical reactions should be considered in the excited, rather than ground, electronic state.

Thus, the catalyst can be considered as a $[CuCl_4]^{2-}/[CuCl_2]^-$ couple formed in situ by oxidation of the substrate and reduction of the diazo cation. The presence of both the oxidized and reduced forms of the catalyst is necessary for the elimination of nitrogen, because both these forms actively participate in the process:

$$ArN_2^+ \xrightarrow{[CuCl_4]^{2-}} [ArN_2^+]^*,$$

$$[ArN_2^+]^* \xrightarrow{[CuCl_2]^-} Ar^\bullet + N_2 + [CuCl_4]^{2-}.$$

To conclude, the interaction of the phenyldiazonium cation with the catalyst can be presented as follows. Due to thermal motion, passing of atoms through a point with the C–N bond length close to 1.6 Å may induce the 1T $\pi(b_1) \rightarrow \sigma^*_{CN}$ transition, which in this case becomes the most energetically favorable. In this point, the ligand-to-metal electron donation will involve the σ^*_{CN} orbital, and the reduction of the triplet diazo cation will facilitate the nitrogen elimination.

CONCLUSIONS

(1) Elimination of the nitrogen molecule from the diazo cation is impossible in the ground state because of the bonding (with respect to the C–N bond) character of the lower unoccupied molecular orbital of phenyldiazonium. At the same time, triplet excitation of the diazo cation with the electron transfer to the σ^*_{CN} orbital will yield a structure capable of nitrogen elimination.

(2) In the mechanism of the ligand-to-metal and metal-to-ligand electron donation in the Meerwein reaction, the spin catalysis is a decisive factor in formation of the triplet state of the diazo cation. The tetrahedral complex $[CuCl_4]^{2-}$ plays a key role as a structure in which the 3*d* orbital fits, like a key to a lock, the σ^*_{CN} orbital of the diazo cation. The role of the oxidized and reduced forms of copper in the catalytic process was substantiated.

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