

Reaction Behavior of Quinone Carbene in C-S Bond Construction: From Chemical Mechanism to Catalyst Regulation

Weiqi He

*Institute of Chemistry, Jinan University, Jinan, China
weiqi3329@gmail.com*

Abstract. Organic molecules containing C-S bonds have crucial application value in the field of medicinal chemistry and functional materials. However, traditional synthetic methods, such as thiol nucleophilic substitution, are often restricted by some factors, for instance, the reaction conditions are relatively harsh, the functional group tolerance is not good, and there is a risk of oxidation of sulfur atoms. The quinone-mediated C-S bond construction method provides a new approach for the gentle and efficient direct construction of C-S bonds. Its core mechanism is as follows: In this study, transition metals and diazoquinones are combined to catalyze the formation of highly active carbon intermediates. Due to their relatively strong electrophilicity, these intermediates can directly react with sulfides to form C-S bonds. The reaction requires no substrate preactivation and can proceed at room temperature under an inert atmosphere, effectively avoiding side reactions such as sulfur oxidation. Reaction conditions including catalyst type, solvent system, and reaction temperature affect the chemoselectivity and regioselectivity of the products. This study aims to overcome the limitation of poor regioselectivity control in traditional thiol nucleophilic substitution reactions, provide efficient and green new strategies for the precise synthesis of sulfur-containing functional molecules, and further expand the application potential of carbene reactions in the synthesis of complex molecules.

Keywords: Carbine reaction, C-S bond, Diazoquinone

1. Introduction

Carbon-Sulfur (C-S) bond-forming reactions and related methodologies C-S bond-forming reactions play an important role in organic synthesis and materials science. Compounds containing C-S bonds exhibit diverse structures and broad applications, and are widely present in nature and daily life [1]. For example, penicillin-class antibiotics such as Penicillin G and Amoxicillin have a core structure formed by the fusion of a β -lactam ring and a sulfur-containing heterocycle. The sulfur atom in these molecules not only enhances antibacterial activity but also affects drug stability. Similarly, cephalosporin-class antibiotics like Cefalexin and Ceftriaxone possess a structure where a β -lactam ring is fused with a six-membered sulfur-containing heterocycle. Here, the sulfur atom influences the antibacterial spectrum and endows the drugs with β -lactamase resistance. In both classes of

drugs, the β -lactam ring and the sulfur-containing heterocycle act synergistically: the inhibition of bacterial cell wall synthesis is achieved through the dynamic cleavage and reformation of the C-S bond, and the antibacterial activity directly depends on the electronic effects exerted by the sulfur atom.

In precious research, the poisoning effect of sulfur on catalysts commonly used in such reactions resulted in limited substrate scope and low yields for these reactions. This drawback has restricted the application of the reaction in the preparation of biologically active sulfides or sulfides involved in the synthesis of bioactive compounds.

To mitigate this poisoning effect, research efforts have shifted toward exploring different types of catalysts. A broad class of reaction systems catalyzed by transition metals has thus been established. After decades of continuous research and iterative improvements, multiple mature and reliable methodological systems have been developed in this field.

Diazoquinones undergo catalytic decomposition by transition metals to form carbene intermediates. Carbenes exhibit high electrophilicity and can react directly with sulfur nucleophiles without the need for preactivation steps. Furthermore, such reactions typically proceed at room temperature under an inert atmosphere, effectively preventing the oxidation of sulfur atoms to byproducts such as sulfoxides or sulfones. This advantage makes the strategy of transition metal-catalyzed quinone carbene highly attractive for C-S bond formation reactions.

2. Structure and reactivity of quinone carbene

Common carbenes, such as dichlorocarbene and methylene carbene, typically exist as transient reactive species. It was not until the late 20th century that chemists successfully isolated stable carbenes under ambient conditions, such as N-heterocyclic carbenes (NHCs).

2.1. Electronic structure and electrophilicity

Carbonene is a highly active neutral intermediate with a divalent carbon atom and two non-bonding electrons. The structure of quinone carbenes has its unique features. Its center is directly connected to the quinone ring. Compared with traditional carbonene, the lone pair of electrons at the center of carbonene can form p - π conjugation with the π system of the quinone ring. This will lead to the delocalization of electrons. Because the quinone ring is a strong electron-withdrawing system, it can stabilize and significantly reduce the energy of the empty p orbital at the center of the carbonene. This electron delocalization from the electron-rich quinone part to the entire molecular framework keeps the carbon-carbon in a highly electron-deficient state. This unique electronic structure gives quinone carbonenes a strong electrophilicity, and the low-lying lowest unoccupied molecular orbital is conducive to the effective acceptance of electron-rich substances. This makes quinone carbenes highly effective in nucleophilic attack reactions.

2.2. Carbene generation pathways

In the process of transition metal-catalyzed decomposition of diazo compounds, metal catalysts represented by $Rh_2(esp)_2$ are the key to this process. The research by Yan demonstrated that the transition metal catalyst coordinates with the diazo group in the diazoquinone molecule, followed by the synchronous and efficient release of nitrogen gas [2]. After the nitrogen gas escapes, a high-energy rhodium-quinone carbene metal carbene intermediate is formed. This metal carbene intermediate features a unique electronic structure with a carbene center conjugated to a quinone

ring, demonstrating extremely strong electrophilicity. It is precisely this high reactivity that enables it to be immediately captured by the nucleophiles in the system. Metal carbene intermediates, due to their reactive nature, can directly react with sulfur-containing organic compounds to form thioylides. Subsequently, depending on the side chains and ligands, different selective rearrangement reactions will occur. Unlike previous reaction pathways, this catalytic path has mild conditions and is a reliable strategy for utilizing quinone carbenes.

3. Quinone carbene-mediated C-S bond formation mechanism

3.1. Transition metal-catalyzed pathway

Transition metals efficiently stabilize the highly reactive intermediates by coordinating their empty d orbitals with diazo ligands. In current research, dinuclear rhodium catalysts represented by Rh₂ series complexes exhibit the most prominent performance, and their catalytic cycle can be summarized into three key steps:

First, coordination between the metal center and the diazoquinone promotes nitrogen extrusion, generating a stable metal carbene intermediate, efficiently decomposing the diazoquinone and forming a stable metal carbene intermediate. The core role of the transition metal is that the carbon-nitrogen double bond of the diazoquinone coordinates with the Rh center of the dinuclear rhodium through lone pair electrons to form an Rh₂(II)-diazoquinone complex, avoiding side reactions such as self-dimerization of the quinone carbene [3].

Second, the lone pair electrons of the sulfur atom in the thioether substrate directionally attack the active carbon center of the metal carbene, forming a sulfur ylide intermediate or directly undergoing a concerted insertion reaction. During this process, the steric hindrance of the catalyst ligand neither overly blocks the Rh active center. Spatial exclusion can also prevent the aggregation and inactivation of active centers. This enables diazoquinone to efficiently decompose into the quinone carbene-Rh intermediate. Meanwhile, the electronic effect of the intermediate itself also plays a role, increasing the difficulty of the occurrence of side reactions. After the intramolecular electron rearrangement, the quinone group couples with the sulfide substituent to form a C-S bond, and the catalyst enters the next cycle.

Transition metals not only reduce the activation energy of the reaction, but also enhance the selectivity of the reaction through weak interactions such as hydrogen bonds and coordination with the substrate. The construction of C-S bonds with high regioselectivity and chemical selectivity can be achieved under mild conditions. It provides efficient and reliable method support for the synthesis of important sulfur-containing compounds such as diaryl sulfides.

3.2. Regioselectivity and chemoselectivity of thioether insertion reactions

3.2.1. High regioselectivity

Carbenes tend to insert into specific positions, generating structurally clear products. Reaction selectivity is achieved through the electronic effect of transition metals and the steric hindrance of ligands. On the one hand, the valence state change of the metal center can guide the substrate to react according to a specific mechanism. As pei's work shows, manganese drives a specific catalytic mechanism of oxidative addition - reductive elimination through an oxidation cycle of 0 valence → high valence → 0 valence, guiding alkyl halides to couple directionally with sulfur radicals, rather than the traditional nucleophilic attack - leaving group dissociation mechanism of SN₂ reactions [4].

On the other hand, the spatial structure of ligands (such as the naphthylimide group of $\text{Rh}_2(\text{S-NTTL})_4$) can stabilize the dominant transition state through non-covalent interactions like hydrogen bonds and π - π stacking, which can be used to regulate reaction pathways and achieve high regioselectivity and enantioselectivity

3.2.2. High regioselectivity

Transition metals only directionally activate the coupling between alkyl halides and thiyl radicals, excluding side reaction pathways such as $\text{S}_\text{N}2$ and β -H elimination. The reaction completely stagnates in the absence of transition metal catalysis.

In Pei's system, thioformates undergo directional decomposition into thiyl radicals and carbon monoxide (CO) under manganese catalysis, avoiding the formation of heterogeneous sulfur species such as sulfide anions [4]. Moreover, thiyl radicals only react with Mn-alkyl intermediates without interacting with other functional groups, when replaced with thiols or sodium sulfides, the yield decreases significantly. As a redox-neutral system, it does not require strong acids, strong bases, external oxidants, or ligands. The mild reaction condition at 70 °C prevent ester hydrolysis, hydroxyl dehydration, and over-oxidation of thioethers, and substrates containing ester groups, hydroxyl groups, and heterocycles can all retain their functional groups intact.

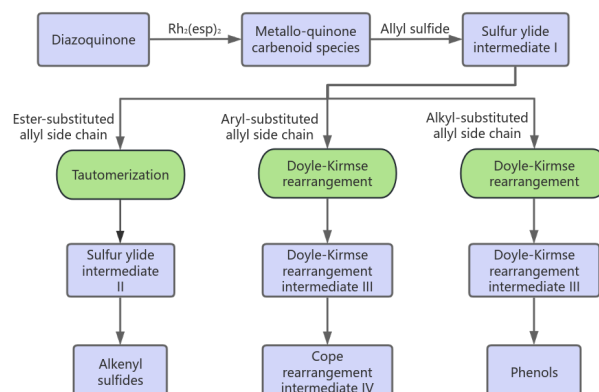


Figure 1. Transition metal-catalyzed quinone carbene formation pathway

4. Optimization of reaction conditions conclusion

4.1. General reaction factors affecting reaction rate and selectivity

4.1.1. High regioselectivity

Catalyst loading directly affects reaction efficiency. Excessive catalyst is prone to agglomeration, leading to reduced activity and increased reaction costs. Studies by Zhang et al. have shown that a transition metal catalyst with a loading of 5 mol% can provide sufficient active sites to effectively promote the deamination (N_2 elimination) of diazoesters to form metal carbenoid intermediates [5].

4.1.2. Reaction temperature and environment

Transition metal-catalyzed reactions are usually carried out under inert gas protection and mild conditions: high temperatures are likely to cause side reactions such as diazoquinone decomposition

and substrate isomerization, while the energy barriers of most transition metal catalytic systems can be overcome at room temperature. Mild conditions not only avoid the risk of side reactions but also achieve efficient conversion of diazo-containing substrates.

4.2. Structural and reaction path differences of transition metal catalysts

The structural characteristics and reaction mechanisms of transition metal catalysts directly determine the type of intermediates, thereby dominating the product orientation. The differences between Pd and Rh catalysts are particularly significant:

4.2.1. Reaction path of Pd catalysts

In Pd-catalyzed systems, the dehydration energy barrier of intermediates is extremely high, making dehydration reactions difficult to occur at room temperature. Instead, intermediates tend to form thermodynamically stable quaternary ammonium α -imine products through proton transfer. Meanwhile, the square planar coordination structure of Pd^{2+} exhibits steric hindrance, which further inhibits intramolecular cyclization reactions. In experiments, square planar coordinated Pd catalysts such as $\text{Pd}(\text{cod})\text{Cl}_2$ only produce imine products without cyclized by-products [6].

4.2.2. Reaction path of Rh catalysts

Rh catalysts rely on non-covalent interactions between ligands and substrates. Weak hydrogen bonds and π - π stacking and other effects preferentially promote the C-O cyclization and subsequent C-C cyclization of the intermediate. Moreover, the weak electrophilicity of Rh catalysts significantly inhibits the dehydration pathway, ultimately leading to the formation of diastereoselective bicyclic furopyrrolone products [7]. Relevant mechanistic studies have been verified by experiments and DFT calculations [5].

4.3. Influence of halogen substituents on reaction efficiency

Halogen substituents significantly regulate the efficiency of palladium, rhodium, and other catalysts in diazoquinone reactions through the combined effects of electronic effects and steric hindrance, with the influence rules varying depending on catalyst characteristics: for palladium catalysis, it is a competitive balance between electronic effects and steric hindrance, while for rhodium catalysis, it mainly relies on steric hindrance effects. This provides important references for the structural design of reaction substrates.

4.3.1. Influence on palladium-catalyzed systems

Electron-withdrawing halogens such as F and Cl can enhance the nucleophilic activity of carbonyl groups, resulting in a reaction yield of over 70% for aryl aldehydes with F substituents. However, the large steric hindrance of ortho-substituted Br and I causes repulsion with the square planar coordination structure of Pd, leading to a significant decrease in yield. In addition, Br^- in PdBr_2 can stabilize intermediates through halogen-halogen interactions, further optimizing reaction efficiency [6].

4.3.2. Influence on rhodium-catalyzed systems

Steric hindrance plays a dominant role in rhodium-catalyzed systems: ortho-substituted halogens hinder the weak hydrogen bonds and π - π stacking between ligands and substrates, leading to a decrease in the yield of bicyclic products; para-substituted halogens have little effect on yield and selectivity due to their small steric hindrance. Relevant studies report on rhodium-catalyzed spirocyclization reactions [8].

5. Applications of quinone carbenes in materials science

5.1. Sulfur-containing functional molecules

Quinone carbenes, enabled by transition metal catalysis, construct C-S bonds with high reactivity and selectivity, emerging as key intermediates in the preparation of sulfur-containing functional molecular materials. Relying on transition metal-catalyzed C-S bond formation reactions, sulfur atoms or sulfur-containing heterocycles can be precisely introduced, imparting materials with special properties such as electron transport, photoresponsiveness, and biocompatibility.

Under mild conditions mediated by blue LED, quinone-derived photogenic carbenes can undergo directional reactions with sulfur-containing fluorophore precursors - among which thioylide, as an efficient carbene capture agent, forms stable intermediates by nucleophilic attack on the carbene active center, and ultimately generates thioquinone derivatives. This process is consistent with the reaction principle by which blue LEDs promote the coupling of carbene precursors and thioylide. The generated thioquinone derivatives combine the excellent electron transport capacity of quinone rings with the unique photoresponse characteristics of sulfur atoms, and the fluorescence quantum yield can reach over 80% [9,10].

In terms of biocompatible materials, AgNO₃-catalyzed C-S bond formation between quinone carbenes and cysteine derivatives yields sulfur-containing quinone molecules. These molecules can balance antibacterial activity and cytocompatibility through interactions between sulfur atoms and biomolecules, holding promise for application in medical antibacterial coatings [11,12].

Additionally, quinone carbene-mediated sulfur-containing crosslinking reactions can prepare self-healing materials with dynamic disulfide bonds. The ability of these bonds to break and recombine allows the materials to rapidly recover their performance after damage, making them suitable for encapsulation layers in flexible electronic devices [13].

In late-stage modification of bioactive molecules with high reactivity and functional group compatibility, quinone carbenes have emerged as key intermediates for the precise construction of C-S bonds in the late-stage modification of bioactive molecules. They are especially suitable for the modification of drug molecules and natural products containing quinone skeletons or those into which quinone structures can be introduced.

In transition metal-catalyzed systems, when Rh₂(oct)₄ is used as the catalyst, quinone carbenes can react with peptide drugs containing cysteine structures—via the hydrogen atom transfer (HAT) pathway from the S-H bond of thiols to quinone carbenes, precisely introducing thioquinone structures into peptide side chains. This not only enhances the antioxidant stability of the peptides but also avoids disrupting their target-binding conformations [14]. The natural anti-cancer molecule lapatol containing naphthoquinone skeleton, under the catalysis of Ir (III) complex, reacts quinone carbene with thiophene thiol to form thioether-substituted naphthoquinone, and the tumor selectivity of the modified molecule is significantly enhanced [15].

In the optimization of antibacterial drugs, Ru catalyzes the C-S bond construction of quinone carbene and phenanthrophenol, which can introduce a sulfide group at the quinone ring 2 position of β -keto ACP synthase III inhibitors, enhancing the hydrophobic binding between the drug and the active center of bacterial enzymes [16]. In addition, AgNO_3 catalyzes the reaction between quinone carbenes and cysteine derivatives, which can construct C-S bonds in bioactive molecules, taking into account both antibacterial activity and cytocompatibility [17].

The advantages of such modifications lie in mild reaction conditions and high selectivity, which avoid damaging the key functional groups of bioactive molecules. This provides an efficient pathway for drug molecule optimization and functional expansion of natural products.

6. Current challenges and future directions

6.1. Catalyst poisoning and deactivation

In industrial catalytic scenarios, SO_2 is the key factor causing the poisoning and deactivation of noble metal catalysts. The catalyst poisoning and deactivation induced by SO_2 can be categorized into structural damage at the chemical level and adsorption blocking at the physical level.

Sulfides pose a risk of coordination poisoning to transition metal catalysts (especially the noble metal Rh), which may lead to catalyst deactivation. Even the optimized $\text{Rh}_2(\text{esp})_2$ system is susceptible to poisoning and deactivation in long-term or specific applications [18].

The root cause of poisoning in traditional Pd-based catalysts lies in the strong interaction between SO_2 and metal active sites [19]. SO_2 will be strongly adsorbed onto the surface of Pd through the metal (d)- $\text{SO}_2(\pi^*)$ feedback bond. While occupying the active site, it may also react with Pd to form stable sulfides or sulfates, leading to the "permanent deactivation" of the catalyst. Traditional Pd catalysts are completely deactivated in an atmosphere of 100 ppm SO_2 for 10 to 20 hours. This strong adsorption is essentially due to the formation of stable coordination bonds between the lone pair of electrons of sulfur atoms and the D-orbital electrons of precious metals, blocking the contact channels between reactants and active centers. Meanwhile, SO_2 can induce phase transitions in the active components, such as converting active metals into catalytically inert sulfide phases, resulting in permanent loss of the active sites of the catalyst.

In addition, SO_2 is converted into sulfate and sulfite species during the catalytic reaction. At the microscopic level, these substances will deposit on the surface of the catalyst to cover the active sites. Sometimes it may also diffuse into the bulk phase of the carrier, destroying the crystal structure of the catalyst and the performance of redox. Under the combined effect of surface blockage and structural damage, the catalyst will be deactivated. Even after the reaction is completed and it is removed from the sulfur-containing atmosphere, its activity is difficult to recover [20,21].

6.2. Green catalytic systems

Catalytic metals are still needed on a large scale in industrial production so far. Due to the reliance on precious metal catalysts such as rhodium, the production cost is high. Transition metal catalysts are also vulnerable to sulfide coordination poisoning, leading to deactivation and further increasing costs. Therefore, developing metal-free catalytic systems is the key to lowering the threshold for industrialization.

Metal-free systems do not rely on noble metal catalysts such as transition metals. The main methods include organic catalysis, photo-induced electron transfer, and electron donor-acceptor

(EDA) complex mediation, etc. These methods can directly activate the substrate to react, avoiding the problems of metal residues and sulfide poisoning. In Li's work, the photosensitivity of diazoquinone itself and the construction of EDA complexes were utilized. Under visible light irradiation, the substrate can generate quinone carbene intermediates and sulfur-containing free radicals. This path can efficiently achieve the insertion of carbon-sulfur bonds without the need for additional metal catalysts [16].

The development of metal-free catalytic systems has addressed the costs associated with transition metal dependence and the issue of catalyst poisoning. At the same time, it also takes into account both reactivity and selectivity. In addition, electrochemical, photochemical and other pathways also have considerable potential. However, due to the inherent tendency of diazoquinone to decompose easily, the safe conversion methods for other paths still need to be further studied

6.3. Combination of theoretical calculations and mechanism research

Density functional theory (DFT) is a core tool in computational chemistry. Its core strength lies in using electron density to calculate the ground-state properties of electronic systems (such as molecules and catalyst intermediates). This method replaces the one that uses complex wave functions. While simplifying calculations, it ensures accuracy and is now widely applied in fields such as catalysis, materials, and organic synthesis. It can assist in substrate design and theoretical calculation to reveal the reaction mechanism.

In the transition metal-catalyzed diazoquinone-mediated carbon-sulfur bond insertion reaction, the core value of DFT lies in the analysis of the reaction mechanism and the confirmation of feasible paths through the calculation of activation energy: by quantifying the dynamic coordination behavior, electronic distribution characteristics, and reaction energy barriers of transition metals and diazoquinones at each step, the rate-limiting step of carbon-sulfur bond insertion is clarified, providing theoretical support for catalyst design.

Similar prototypes can already be seen in the relevant neighborhoods. In Li's work, DFT calculations reveal the "X-type - L-type" dynamic coordination switching between the diazoquinone (DQ) ligand and the Ni catalyst - in the migration insertion step, DQ binds to Ni (II) as an X-type semiquinone radical anion. Reduce the insertion energy barrier from 31.1 kcal/mol to 23.1 kcal/mol; In the oxidative addition step, L-shaped ligands are converted to bind Ni (I), reducing steric hindrance. This DFT research framework can be directly transferred to the diazoquinone system, providing a mechanism reference for the carbon-sulfur bond insertion reaction mediated by it.

In the future, it is necessary to combine the characteristics of diazoquinone substrates, optimize the selection of functionals and base groups, and further achieve precise simulation of reaction mechanisms and directional design of catalyst structures. Through mechanism research to guide substrate design and condition optimization, precise regulation of C-S bond construction sites and stereochemistry is achieved.

7. Conclusion

This study focuses on the C-S bond formation reaction mediated by quinone carbenes. Transition metals represented by Rh and Pd are the core driving forces of this type of reaction. Among them, the Rh catalyst, due to its relatively weak electrophilicity and the ability to form non-covalent interactions, is more inclined to initiate cyclization reactions. The Pd catalyst has a square-planar coordination structure, which has a higher energy barrier during dehydration and thus is more likely to generate linear products. After optimization, the optimal conditions for the reaction are a catalyst

dosage of 5 mol%, a low-polarity solvent, and a mild inert environment. In addition, the composition of the side chains also affects the rearrangement of the reaction, where the halogen substituents influence the reaction due to electronic effects and steric hindrance effects. The activity of the reaction can be regulated through these.

At present, this method has been successfully applied in many places. For instance, the preparation of functional materials such as light-responsive thioquinone compounds and self-healing polymers, as well as the post-modification of drugs. This method can effectively enhance the stability and selectivity of bioactive molecules. However, the current research is facing a challenge: precious metal catalysts are prone to being "poisoned" by SO₂. Therefore, the development of green catalytic systems becomes particularly urgent. In the future, it can be planned to focus on the research and development of low-cost metal-free or non-precious metal catalysts. By combining DFT theory and experiments, the reaction mechanism can be made clearer, and then its application can be expanded to the field of electrochemical material transformation. Overall, this research has laid the foundation for the efficient and highly selective construction of C-S bonds and can also promote the synthesis of sulfur-containing compounds towards a more sustainable catalytic direction.

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