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CIDNP Study of Photoinduced [2+2] Cycloadditions (the Paterno-Büchi Coupling) of Arylacetylenes and Quinone

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Abstract: CIDNP techniques were applied to study the mechanism of photocycloadditions of 2-chloro-5-methoxybenzoquinone **1** with arylacetylenes **2-5** in benzene-d_6 and acetonitrile-d_6 respectively.

Keywords: Paterno-Büchi reaction, 1, 4-biradicals, photo-CIDNP, arylacetylenes, quinones.

The photoinduced [2+2] cycloaddition of an olefin to a carbonyl center, also known as the Paterno-Büchi reaction, is a convenient way to prepare oxetane with high regio- and stereoselectivities. Most importantly, the range of carbonyl compounds has been extended to enones, quinones, diones *etc*., and the alkenes, dienes, and acetylenes as the olefinic counterparts. The process can be viewed as a variant of the Paterno-Büchi reaction[1]. It is believed that in all postulated mechanisms, the formation of a 1, 4-biradical is a crucial intermediate *prior to* cyclization. Photoinduced reactions of aromatic ketones and quinones with diphenylacetylene are known to give quinone methides and α, β-unsaturated ketones, respectively, *via* the unstable oxetene intermediates[2] formed by [2+2]cycloaddition of the carbonyl C=O band with acetylenic C≡C bond[3].

A convenient means to study reactions *via* radical pairs and distinguish them from reactions involving exciplexes and short-chain biradicals only is provided by measurements of chemically induced dynamic nuclear polarizaion (CIDNP)[4].

In this work, CIDNP techniques were applied to study the mechanism of photocycloadditions of 2-chloro-5-methoxybenzoquinone **1** with arylacetylenes **2-5** by direct photoexcitation of quinone **1** at λ_{exc}=365 nm. The ^{1}H CIDNP experiments were carried out by using 1000 W high pressure Hg lamp as the light source, and the concentrations of reactants were 0.02 mol/L. The following requirements are met in these donor-accepter systems. At the excitation wavelengh, the light is absorbed exclusively by **1**. UV/vis and ^{1}H NMR could not provide the information of formation of ground state complexes. The intersystem cross of the quinone **1** to its triplet state($\varphi_{isc}\approx1$)[5] occurred very rapidly[6].

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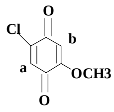
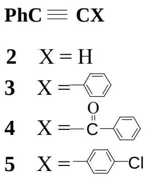
Hence **1** could not be quenched to appreciable degree with the concentrations of **2-5** used in the experiments.



1

aryacetylenes

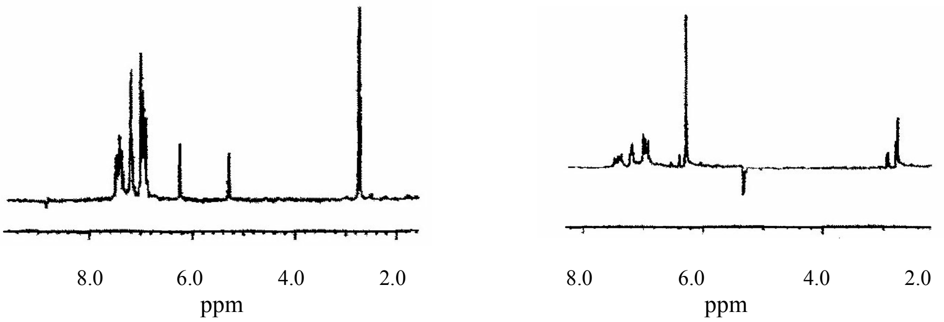


Results and Discussion

The previous studies of 2, 6-dichlorobenzoquinone (DB) with (diaryl) acetylenes at λ_{exc} =355 nm resulted in single-electron transfer (SET) from the acetylene to the strong quinone acceptor DB. Direct SET led the formation of ion-radical pairs or free solvated ions[3b] after the cycloaddition of the carbonyl C=O bond with acetylenic C≡C bond. If a methoxy group at 5 position instead chloro at 6 position, the relatively weak electron acceptance of methoxy group could lead the different reaction pattern and intermediates in our system from those of DB. The following CIDNP results provided the proof of the above assumptions.

Upon irradiation (365 nm) of **1** and **2-5** in benzene-d_6, strong nuclear spin polarizations were observed in all cases (**Figure 1**): Absorption (A) of proton **a** enhanced at 6.30 ppm**,** and emission (E) of proton **b** at 5.30 ppm respectively. However, no obvious polarizations were observed in acetonitrile-d_6.

Figure 1 ^{1}H photo-CIDNP spectrum of reaction of **1** and **2** in benzene-d_6, dark (left), during irradiation (rigt)



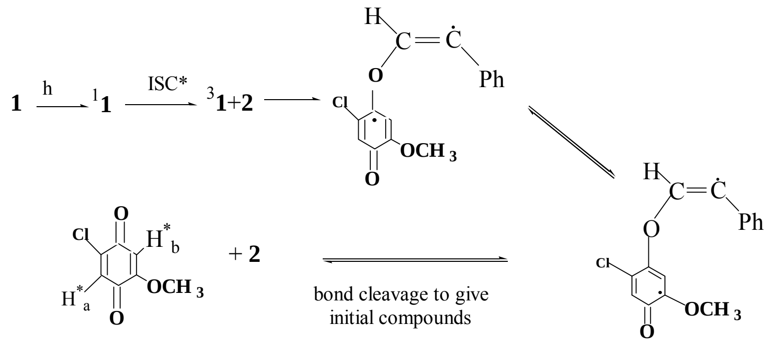
Arylacetylenes **2-5** are relatively weak electron donors, the free energy change ΔGET for electron transfer (SET) between the arylacetylenes and the triplet **1** can be estimated by Weller equations[7]. **Table 1** shows the estimated ΔGET values between **1** and **2-4**. In benzene, arylacetylenes **2-4** all have positive ΔGET value for electron transfer with $^3\mathbf{1}^*$. Since **5** should have higher oxidation potential than **3**, it should also have more positive ΔG_{ET} value. So the SET process should not be involved in these reactions, and ion-radical pair formation is thermodynamically unfeasible, and 1, 4-biradicals are formed as the intermediates. This process was showed in **Scheme 1**.

Table 1 Free-energy change for SET between $^3\mathbf{1}^*$ and arylacetylenes **2-4**

Arylacetylene	$E_{1/2}^{ox}$(V *vs*. SCE)	Solvent	ΔG_{ET} (Kcal/mol)
2	2.04[10]	C_6H_6	16.4
2	2.04[10]	CH_3CN	6.3
3	1.49[11]	C_6H_6	3.7
3	1.49[11]	CH_3CN	-6.4
4	1.53[11]	C_6H_6	4.6
4	1.53[11]	CH_3CN	-5.5

The reduction potencial of quinone **1** is -0.46V[11], and E_T is the triplet energy of **1**≈ 50kcal/mol[11].

Scheme 1



*denotes the intersystem cross

The observation of CIDNP effects provides direct evidence for the intermediate of short-lived biradicals, which are not easily detected by other techniques. There are two kinds of CIDNP from biradicals[8]. One is similar to CIDNP from freely diffusing radical pairs based upon mixing of the electronic singlet state with the triplet ($S\text{-}T_0$ mixing), induced by the hyperfine interaction of nuclei with electrons. In $S\text{-}T_0$ mixing, both enhanced absorption and emission are to be expected. The other type is due to $S\text{-}T_-$ mixing, which results in purely emissive NMR spectra of the products. The CIDNP effects observed in our experiment showed the $S\text{-}T_0$ mechanism, which can be simply explained by Kaptein's rule[9].

There is a critical requirement of chain length, short-chain 1,4-biradicals rarely can give rise to CIDNP effects. The quick transformation to 1,6-biradical can explain the polarization in our experiments more reasonably. To apply Kaptein's rule to the reaction of **1** with **2** for CIDNP net effects,

$$\Gamma_i = \mu\ \varepsilon\ \mathrm{sgn}\ \Delta g\ \mathrm{sgn}\alpha_i$$

μ = +, owing to the triplet multiplicity of the excited **1**. For escaping product, ε= -. The Δg for **1** is positive. The coupling constant α is negative for H_a and positive for H_b in delocalized radicals, where for α-H, $\alpha < 0$; and for β-H, $\alpha > 0$. We find that

$$\Gamma_a = + - + - = + \text{ (A)} \qquad \Gamma_b = + - + + = - \text{ (E)}$$

The radical scavenger PBN was used to verify the exit channel of products. The polarization is suppressed with the increasing of the PBN concentration. This also showed that the products are formed after escaping from the cage.

In acetonitrile, the absence of obvious polarization indicated that the reducing of the stability of the excited quinone and the drastic solvent polarity effect on the reaction, which made further dissociation of the triplet ion-radical pairs, and thus the suppressed intermolecular coupling leading to the cycloaddition, could all contribute to the lack of polarization.

The detail mechanism is in further investigation.

Acknowledgment

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