Pergamon

Tetrahedron Vol. 50, No. 4, pp. 1199-1210, 1994
Copyright © 1994 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0040-4020/94 $6.00+0.00

0040-4020(93)E0074-P

Photoinduced Addition Reactions of Chloranil with Alkenes —Factors Influencing the Reaction Site

Jian–Hua Xu*, Yi–Lin Song, Zhao–Guo Zhang, Long–Cheng Wang, Jian–Wei Xu
(Department of Chemistry,Nanjing University,Nanjing 210008, China)

Abstract: Photoinduced addition reactions of chloranil (CA) with allyl ethyl ether **1**, methyl methacrylate **2**, vinyl acetate **3**, styrene **4**, α–chloro–styrene **5**, and α, p–dichlorostyrene **6** gave cyclobutane products **10** to **15** respectively. Similar reaction of CA with indene **7** and (*E*)–β–bromostyrene **8** gave oxetanes **16** and **17** respectively. Products of photoinduced addition of CA with cyclohexene **9** are solvent dependent: **18** in benzene, **19** in acetonitrile, and **18** and **19** both in dichloromethane. The role of SET process in determining the reaction site are discussed.

Photoinduced cycloaddition reactions of quinones with alkenes have been an area of continuous interest in organic photochemistry[1,2]. Depending on the structure of the quinones and the alkenes, the reaction can take place at either the carbonyl or the ethene double bond of the quinone moiety. The reaction modes and scope of the photocycloaddition of the parent benzoquinone (BQ)[3-7] and naphthoquinone (NQ)[8-11] with alkenes have received intensive investigation, as have the reactions of some of the halo–substituted naphthoquinones[12-15] from which novel synthetic reactions have been developed. Recently, one of the major concern in the area of quinone–alkene photochemistry is to provide mechanistic rationalization of the reaction site and regioselectivity seen in these reactions[7,11,12,15,16]. The photoinduced addition reactions of chloranil (CA) with different alkenes were first investigated by Schenk[17], Bryce–Smith[18], Barltrop[8] and their coworkers and were among the first reported quinone–alkene photoreactions although since then they have not received as much attention as BQ and NQ[19,20].

In the visible region of the electronic spectrum of CA there is a forbidden π–π^* absorption at 367nm with an ε value of $\sim 250\text{M}^{-1}\ \text{cm}^{-1}$ in acetonitrile, chloroform or alcohols. In solvents with donor ability as benzene, this band is largely obscured by the long wavelength absorption of ground state charge transfer complex (CTC) between CA and the solvent. The n–π^* absorption which is clearly seen in the spectrum of BQ can not be observed in CA's spectrum and is believed to have been blue–shifted to be submerged underneath the

$\pi\pi^*$ absorption[21]. Considering the larger singlet–triplet splitting of the $\pi\pi^*$ state as compared with $n\pi^*$ state, the lowest energy triplet state of CA should be the $\pi\pi^*$ state well seperated from the $n\pi^*$ state. The large singlet–triplet energy difference of the $\pi\pi^*$ state and the high intersystem crossing rate constant ($\sim 3 \times 10^{10}$ s^{-1} [22]) which is higher than diffusion controlled bimolecular rate constant in solution indicate that, reactions of the excited CA should always be from the $\pi\pi^*$ triplet state. On the other hand, CA has a reduction potential of −0.02V (SCE)[23] and is one of the most strong electron acceptors of all quinones. This unique combination of distinct electronic configuration of triplet excited state and the strong acceptor ability makes us to believe that CA should be a good model compound to display the diversity in reaction modes and to search for mechanistic rationalization of the diverse reaction outcomes in quinone–alkene photochemistry. Reported here is the investigation of the photoinduced addition reactions of CA with allyl ethyl ether **1**, methyl methacrylate **2**, vinyl acetate **3**, styrene **4**, α–chlorostyrene **5**, α,p–dichlorostyrene **6**, indene **7**, (*E*)–β–bromostyrene **8** and cyclohexene **9**. In choosing these alkenes, attentions were paid to cover different structural types and oxidation potentials with the aim of gaining insight into the factors that influence the reaction site and regioselectivity.

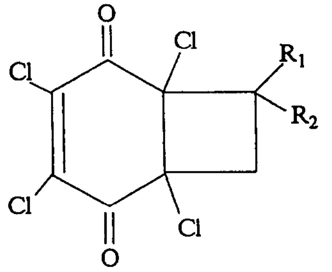
Results and Discussions

All the photolyses were carried out with argon purging in dry solvent with light of wavelength longer than 400nm. Although charge transfer complex formation between CA and donor compounds are common[24–26] and CTC formation of CA with alkenes **2**[27], **4**[28], **7**[29] and **8**[28] have been reported in the literature, electronic spectroscopic measurements show that, the main spectral change caused by CTC formation between CA and alkenes **1–9** occurs in the wavelength range shorter than 400nm, and addition of these alkenes to CA (1×10^{-3}M) solution in CCl_4 in small excess as used in the following preparative photolyses does not cause any significant spectral change in the region longer than 400nm. For these alkenes, CA is selectively excited in the photolyses. For **7**, CTC with CA was measured in CCl_4 solution wich 1×10^{-3}M of CA in the presence of large excese ammounts of **7**. The CTC absorption maximum is at 467nm. Benesi–Hildebrand treatment[30] gave a complex formation constant K_{CT} of $1.1M^{-1}$ and a ε_{CT} of $888M^{-1}cm^{-1}$. Estimation according to the fraction of CA complexed in the presence of 0.034M of **7** and the ε_{CA}, ε_{CT} values showed that, in the following photolysis of the solution of CA (0.02M) and **7** (0.034M), while CA remains the main absorbing species, CTC also absorbs significantly (<20% incident light).

Photolysis of a benzene solution of CA (0.05M) with **1** (0.52M) gave the cyclobutane product **10** in 63% yield together with the photoreduction product tetrachlorohydroquinone (TCH,10%). The yields were based on consumed CA. Similar photolysis in other solvents of different polarity (dichloromethane, chloroform, THF or acetonitrile) also gave **10** as the only addition product. Although **1** was used in large excess, 2:1 addition product in which **1** added to CA's both C = C double bonds was not formed in the reactions.

In the IR spectrum of **10**, the two carbonyl stretching bands appear at slightly different frequencies (1715 and 1690 cm^{-1}). In the ^{13}C NMR spectrum, there are two carbonyl carbon absorptions (180.73 and 180.20 ppm) and two olefinic carbon absorptions (144.70 and 144.39 ppm), indicating the 1:1 cyclobutane structure.

Irradiation of CA with **2** and with **3** in benzene under similar conditions gave cyclobutane products **11** and **12** in 79% and 40% yield respectively. TCH is not formed in these cases.



10: $R_1 = CH_2OC_2H_5$, $R_2 = H$
11: $R_1 = CH_3$, $R_2 = CO_2CH_3$
12: $R_1 = OCOCH_3$, $R_2 = H$
13: $R_1 = C_6H_5$, $R_2 = H$
14: $R_1 = C_6H_5$, $R_2 = Cl$
15: $R_1 = p-ClC_6H_4$, $R_2 = Cl$

Photoreactions of CA with styrene **4** and its α–substituted derivatives **5** and **6** were then investigated. Photolysis of a benzene solution of CA (0.02M) and styrene (0.02M) gave the cyclobutane product **13** in 64% yield. TCH was not formed. In an early study of photoreactions of CA with alkenes by Schenk[17], styrene was reported to give 2:1 cyclobutane products with CA when irradiated in the presence of excess amount of styrene. This is probably the result of further reaction of the 1:1 cyclobutane product with the excess styrene under irradiation.

Similar irradiations of CA with **5** and with **6** in benzene solution afford cyclobutane products **14**(82%) and **15**(82%) respectively.

There are two common features in the infrared spectrum of **10–15** which are diagnostic for the structure of the 1:1 cyclobutane adducts: (i) carbonyl absorption is shifted toward high frequency to 1700–1720 cm^{-1} from 1680 cm^{-1} in CA; (ii) the characteristic C=C stretching band which is at 1560 cm^{-1} in CA[31] is reserved and appears in the region 1550–1570 cm^{-1}.

Alkenes **1** to **6** are relatively weak electron donors, the free energy change ΔG_{ET} for electron transfer (SET) between the alkenes and the triplet CA can be estimated by Weller equations (1) and (2)[32] where $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ stand for the oxidation potential of the alkene and the reduction potential of CA, and E_T is the triplet energy of CA (2.12eV[33]).

in benzene,

$$\Delta G_{ET} = 23.06\left[E_{\frac{1}{2}}^{ox} - E_{\frac{1}{2}}^{red} - E_T + 0.38\right] kcal/mol \tag{1}$$

in acetonitrile,

$$\Delta G_{ET} = 23.06\left[E_{\frac{1}{2}}^{ox} - E_{\frac{1}{2}}^{red} - E_T - 0.06\right] kcal/mol \tag{2}$$

The ΔG_{ET} values estimated by eqns (1) and (2) are the free enthalpy of exciplex formation in benzene and the free energy change for solvent seperated ion pair (SSIP) formation in acetonitrile respectively. The ΔG_{ET} values and the products formed in photoadditions with CA are listed in Table 1. It is seen from Table 1 that alkenes 1–4 all have positive ΔG_{BT} value for electron transfer with $^3CA^*$ in the solvents investigated. Since 5 and 6 should have higher oxidation potential than styrene, they should also have more positive ΔG_{BT} value. These positive ΔG_{BT} values suggest that SET process should not be involved in the reactions of these alkenes with $^3CA^*$.

Table 1. $E(D/D^{+\cdot})$, ΔG_{BT} of the alkenes with $^3CA^*$ and Products of photoadditions with CA.

Alkenes	$E(D/D^{+\cdot})$(V,SCE)	Solvent	ΔG_{BT} (kcal/mol)	Products
1	2.95[a]	C_6H_6	28.4	cyclobutane 10
1		CH_3CN	18.2	cyclobutane 10
2	3.45[b]	C_6H_6	39.9	cyclobutane 11
3	3.10[b]	C_6H_6	31.8	cyclobutane 12
4	2.51[c]	C_6H_6	18.2	cyclobutane 13
5		C_6H_6		cyclobutane 14
6		C_6H_6		cyclobutane 15
7	1.70[b]	C_6H_6	−0.5	oxetane 16
8	2.30[d]	C_6H_6	13.4	oxetane 17
9	2.14[c]	C_6H_6	9.7	cyclobutane 18
9		CH_3CN	−0.5	19
9		CH_2Cl_2	4.6	18+19

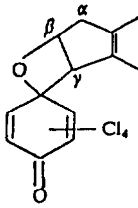
a. estimated by Miller equation[34] from IP (9.62 eV[35]).

b. Reference 36. $E(D/D^{+\cdot})$ (SCE) was obtained by adding 0.3V to $E(D/D^{+\cdot})$ (Ag/Ag^+, 0.01M)[37]

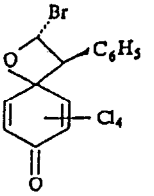
c. Reference 38.

d. Reference 39.

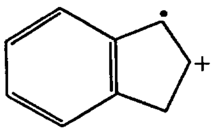
Although styrene derivatives 4 to 6 gave cyclobutane products with CA, it is found that photoinduced reactions of CA with styrene derivatives indene 7 and β–bromostyrene 8 lead to the exclusive formation of oxetane products. Therefore, irradiation of a benzene solution of CA (0.02M) and 7 (0.034M) under simlar conditions as above gave 16 in 50% yield together with TCH (21%). When the photolysis was carried out in chloroform, ethyl acetate or acetonitrile, 16 was also obtained as the only addition product, although with a reduced reaction rate when the polarity of the solvent is increased. The structure of 16 is assigned based on spectral data including a ^1H NMR decoupling experiment. When the β–proton in 16 (triplet at 5.85ppm) was irradiated, the doublet at 4.58 ppm (Hγ) degenerated into a singlet, and the dd splitting at 3.40 ppm (one of the Hα) degenerated into a doublet. This unambiguously proved the regiochemistry shown in 16 where the oxygen atom is linked to the β carbon atom in indene. Indene has an oxidiation potential of 1.70V (SCE)[36], the ΔG_{BT} for electron transfer with $^3CA^*$ in benzene and in acetonitrile as estimated by Weller equations (1) and (2) are −0.5 and −10.6 kcal / mol respectively. These negative values strongly suggest the involvement of SET process in the oxetane formation reaction. Relevant to this, flash photolysis and photo−CIDNP studies by Rentzepis etc.[40] have shown that in polar solvent as acetonitrile, photoinduced reaction of CA with indene and 1,1−dimethylindene induces SET between $^3CA^*$and the alkenes, resulting in ion radical pair formation. The simultaneous excitation of charge transfer eomplex also induces electron transfer between CA and **7**, although in this case contact ion radical pairs of singlet multiplicity are produced[41−44]. The regiochemistry of the cycloaddition seen in **16** is consistent with that predicted from the indene cation radical structure I where positive charge mainly resides at C_β as suggested by the nucleophilic solvent trapping reaction and theoretical calculation[45,46].



16



17



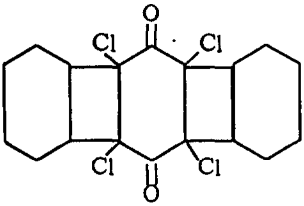
I

Oxetane product formation has also been reported in photoinduced reactions of CA with other low oxidation potential alkenes as barbaralone[19] and benzvalene[20] where electron transfer between $^3CA^*$ and the alkenes were also revealed by flash photolysis[19] or photo−CIDNP[47] studies.

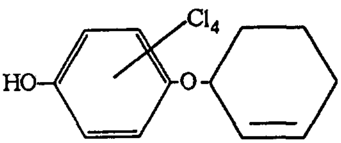
Photolysis of CA with (*E*)− β −bromostyrene **8** in benzene afforded the *trans* − oxetane product **17** in 80% yield. Irradiation in acetonitrile also gave **17** in 78% yield. TCH was not formed. In view of the high oxidation potential of **8** and the large positive ΔG_{ET} values with $^3CA^*$ in benzene and in acetonitrile (Table 1), the oxetane product formation is rather unexpected for a reaction from the $\pi\pi^*$ triplet state of CA without SET process involvement. We have therefore further tested the effect of oxygen as an alkene cation radical scavenger[48,49] on the reaction and found that photolysis of CA with **8** in acetonitrile with constant oxygen purging did not lead to the photooxygenation of **8**, and **17** was still the only product formed. This, in combination with the ΔG_{ET} value, indicated that SET process is not involved in the reaction because otherwise ion pairs formed would be further dissociated and trapped by triplet oxygen in a solvent as polar as acetonitrile.

In photoinduced cycloaddition reactions of CA with alkenes, cyclobutane product formation has previously been reported for several monoalkenes and 1,3−dienes[8,17]. It is interesting to note that all these alkenes are of high oxidation potential and therefore have positive ΔG_{BT} values with $^3CA^*$ if calculated by eqns (1) and (2). Taking as an example of the three alkenes (isobutene, 1,3–butadiene, and 2,3–dimethylbutadiene) investigated by Barltrop[8], 2,3–dimethyl–1,3–butadiene has the lowest $E^{ox}_{1/2}$ (2.13V,SCE[50]) and the ΔG_{BT} with CA in benzene is 9.5kcal / mol. Our results on photoinduced cycloaddition reactions of CA with **1** to **6** and with cyclohexene in benzene *(vide infra)*, as well as the previously reported results cited above clearly show that CA tends to react at its carbon–carbon double bonds with terminal and alicyclic alkenes which have a positive ΔG_{BT} value for electron transfer with $^3CA^*$ *via* non–SET mechanism to give cyclobutane product from its $\pi\pi^*$ triplet state. Oxetane product formation for **8** which also has a positive ΔG_{BT} value is probably caused by steric hindrance toward addition to the dichloro substituted ethene double bond. On the other hand, oxetane product formation for indene is in accord with the previous recognition that efficient oxetane product formation for a carbonyl compound with $\pi\pi^*$ excited state requires a dominant electron transfer interaction with the alkene moiety[51,52].

In the photoinduced reaction of CA with cyclohexene **9**, a drastic solvent polarity effect on the reaction products was observed. When a solution of CA (0.04M) and **9** (0.24M) in benzene ($\varepsilon = 2.3$) was photolysed as above, 2:1 cyclobutane product **18** was obtained in 20% yield together with 42% of TCH. However, irradiation of a solution of CA (0.04M) and **9** (0.24M) in acetonitrile ($\varepsilon = 36.0$) gave the ether–phenol product **19** in 40% yield and TCH in 46% yield. Furthermore, when the photolysis was conducted in dichloromethane ($\varepsilon = 8.93$), cyclobutane **18** (20%) and ether–phenol product **19** (43%) were simultaneously formed together with TCH (16%). Cyclohexene has an oxidation potential of 2.14V (SCE)[38], the free energy change ΔG_{BT} with $^3CA^*$ in benzene and in acetonitrile are estimated by eqns (1) and (2) to be 9.2 and −0.5 kcal / mol respectively. Since in solvent with $\varepsilon > 7$, polar exciplexes tend to dissociate into ion radical pairs, the free energy change for electron transfer between $^3CA^*$ and **9** in dichloromethane can be estimated by eqn. 3[32] where $E^{ox}_{1/2}$, $E^{red}_{1/2}$ and E_T have the same meaning as in eqns. 1 and 2, and ε is the dielectric canstant of the solvent. The ΔG_{BT} obtained is 4.6 kcal / mol.



18



19

$$\Delta G_{BT} = 23.06 \left[E^{ox}_{1/2} - E^{red}_{1/2} - E_T + \frac{2.6}{\varepsilon} - 0.13\right] \text{ kcal / mol} \qquad (3)$$

The large positive ΔG_{BT} value and the formation of product **18** in benzene is consistent with the general trend of cyclobutane formation in photoinduced reactions of CA with alkenes of high oxidation potential without SET involvement. The negative ΔG_{ET} value in acetonitrile suggests that SET process and radical ion pair formation are involved in the reaction and product **19** is most likely formed by sequential electron–proton transfer in the radical ion pair followed by coupling of the semiquinone radical with the allylic cyclohexenyl radical. In the photoaddition of CA with **9** in dichloromethane, two mechanisms compete and products **18** and **19** are both formed.

In summary, photoinduced reaction of CA with terminal alkenes of high oxidation potential and positive ΔG_{ET} value for electron transfer with $^3CA^*$ gave cyclobutane products in accordance with the triplet $\pi\pi^*$ state of CA. However, steric effect may also be important in deciding the reaction site, therefore, for the more sterically hindered **8**, the reaction site is at the carbonyl group of CA and oxetane **17** is the product, although the ΔG_{ET} is still positive. For indene which has a low oxidation potential and a negative ΔG_{ET} value for SET with $^3CA^*$, oxetane product is formed. In photoinduced reaction of CA with cyclohexene, cyclobutane product **18** is formed in benzene, while in acetonitrile, phenol–ether product **19** is formed. This shows that since free energy charge for SET (ΔG_{ET}) is sensitive toward solvent polarity, for alkenes with oxidation potential close to 2V (SCE), reaction products may be solvent dependent as the result of a mechanistic transition from normal non–SET cyclobutane formation reactions in nonpolar solvent to reactions involving SET process and radical ion pair formation in more polar solvents. The photoinduced addition reactions of CA with alkenes are therefore quite diversified both in reaction products and mechanisms, depending on the structure and oxidation potential of the alkenes as well as such reaction conditions as solvent polarity. Further investigations in this area are certainly needed to explore the reaction scope and the relationship between reaction modes and mechanisms.

Experimental

M.p.s were uncorrected. IR(KBr) spectra were taken with a Shimadzu IR 408 spectrometer. ^1H NMR were taken on a JEOL PMX 60 SI at 60 MHz or a Bruker AM 500 spectrometer at 500 MHz with tetramethylsilane (TMS) as internal standard. ^{13}C NMR were recorded on a Bruker AM 500 spectrometer at 125 MHz with TMS as internal standard. Mass spectra were recorded with a ZAB–HS mass spectrometer (VG). UV spectra were recorded with a Shimadzu UV–240 spectrometer.

Alkenes **1**, **2**, **3**, **4**, **7**, **8** and **9** are commercially available and were purified by distillation before use. Alkenes **5** and **6** are prepared by literature procedure [53]. CA was recrystallized twice from acetone before use. Benzene (AR grade) was dried by sodium. Acetonitrile (CP grade) was first refluxed with phosphorus pentoxide for 2h and distilled, then refluxed with anhydrous potassium carbonate for 2h and redistilled.

Photoinduced Reactions of CA with Alkenes. The light source is a 500W medium pressure mercury lamp in a cooling water jacket which was further sorrounded by a layer of filter solution (10% aqueous sodium nitrite solution, 1cm thickness) to cut off light shorter than 400nm. The solution of CA with the alkene was placed in glass tubes (25 ml each) around the light source to be photolysed under constant dry argon purging. TLC and HPLC were used to monitor the reaction course.

After the photolysis, the solvent was removed *in vacuo,* the photoproducts were separated by column chromatography on silica gel column with petroleum ether (b.p. 60–90℃)–ethyl acetate as eluents.

Irradiation of CA with **1**: A solution of CA (1.23g, 5.0mmol) and **1**(4.5g, 52mmol) in benzene (100ml) was photolysed for 7h to afford unreacted CA (0.237g, a conversion of 81%), product **10** (0.846g, 63%) and TCH (0.100g, 10%).

10: M.p. 80–82℃ . IR(KBr): 2979, 2880, 1715, 1700, 1560, 1440, 1380, 1120, 755, 725, 675cm^{-1}. ^{1}H NMR(CDCl$_3$, 500 MHz, H–H COSY): 0.94 (1H, t, J = 7.0Hz, CH$_3$), 2.96 (1H, dd, J = 13.3, 11.0Hz), 3.03 (1H, dd, J = 13.3, 4.8Hz), 3.13–3.23 (2H, m, CH and 1 / 2 OCH$_2$CH$_3$), 3.29 (1H, dq, J = 7.0, 5.0Hz, 1 / 2 OCH$_2$CH$_3$), 3.35 (1H, dd, J = 10.0, 1.6Hz). ^{13}C NMR (CDCl$_3$): 180.73, 180.20, 144.71, 144.39, 69.52, 67.01, 66.76, 65.22, 47.52, 33.19, 13.85 ppm. MS (m / z): 285(M$^+$–OC$_2$H$_5$, 0.4), 262(1.8), 245(1.3), 216(3.7), 181(5.0).153(2.9), 85(89.1), 57(base). Anal. calcd. for $C_{11}H_{10}Cl_4O_3$:C 39.79, H 3.04. Found: C 39.58, H 3.00.

Irradiation of CA with **2**: A solution of CA (1.00g, 4.1mmol) and **2** (0.980g, 9.8mmol) in benzene (100ml) was photolysed for 9h to give recovered CA (7mg, a conversion of 99%) and product **11**(1.10g, 79%).

11: M.p. 90–91℃ . IR(KBr): 2950, 1710, 1560, 1458, 1310 , 1200, 1150, 1015, 905, 732, 700cm^{-1}. ^{1}H NMR(DMSO–d$_6$): 1.67(s, CH$_3$), 2.68(d, J = 14Hz, 1H), 3.48(d, J = 14Hz, 1H), 3.64(s, 3H) ppm. MS(m / z): 344(m$^+$, 0.4), 309(M$^+$–Cl, 55.1), 277(base), 249(19.5), 244(3.8). Anal. calcd. for $C_{11}H_8Cl_4O_4$: C 38.15, H 2.31. Found: C 38.55, H 2.11.

Irradiation of CA with **3**: A solution of CA (1,23g, 5.0mmol) and **3**(0.865g, 10.1mmol) in benzene (100ml) was photolysed for 8.5h to give product **12**(0.650g, 40.3%). Significant amount (~ 1.0g) of tarry material was also formed during the reaction.

12: M.p. 116–117℃ . IR(KBr): 1750, 1730, 1705, 1570, 1430, 1376, 1220, 1123, 900, 775, 700cm^{-1}. ^{1}H NMR(CDCl$_3$): 2.10(3H, s), 2.88(dd, J = 12, 6Hz), 3.35(dd, J = 12, 6Hz), 5.68(1H, t, J = 6Hz)ppm. MS(m / z): 330(M$^+$, 0.1), 253(33.8), 244(0.2), 224(34.4), 87(base). Anal. calcd. for $C_{10}H_6Cl_4O_4$: C 36.14, H 1.81, Found: C 36.50, H 2.12.

Irradiation of CA with **4**: A solution of CA (1,00g, 4.1mmol) and **4** (0.430g, 4.1mmol) in benzene (150ml) was photolysed for 4h to give unreacted CA (0.579g, a conversion of 42%) and **13** (0.387g, 64%).

13: M.p. 169–171℃ . IR(KBr): 1720, 1690, 1558, 1490, 1430, 1270, 1182, 1090, 780, 690cm^{-1}. ^{1}H NMR(CDCl$_3$): 3.35(2H, m, CH$_2$), 4.60(1H, t, CH), 7.49 (5H, m, Ar–H).

MS(m / z): 313(M^+–Cl, 37.1), 278 (M^+–2Cl, 47.4), 244(3.9), 104(base). Anal. calcd. for $C_{14}H_8Cl_4O_2$: C 48.04, H 2.30. Found: C 47.89, H 2.50.

Irradiation of CA with **5**: A solution of CA (1,20g, 4.9mmol) and **5**(1.25g,9.0mmol) in benzene (120ml) was photolysed for 10h to give recovered CA (0.020g, a conversion of 98%) and **14**(1.515g, 82%).

14: M.p. 126–128℃. IR(KBr): 1700, 1550, 1490, 1450, 1425, 1280, 1260, 1216, 1162, 1120, 738, 690cm^{-1}. ^{1}H NMR($CDCl_3$): 3.76(2H, s), 7.48(5H, s). MS(m / z): 347(M^+–Cl, 28.0), 312(M^+–2Cl, 27.5), 283(12.6), 138(base). Anal. calcd. for $C_{14}H_7Cl_5O_2$: C 43.70, H 1.82. Found: C 44.09, H 2.19.

Irradiation of CA with **6**: A solution of CA (1.23g, 5.0mmol) and **6** (1.62g, 9.4mmol) in benzene (100ml) was photolysed for 6h to give **15**(1.73g, 82%).

15: M.p. 129–130℃. IR(KBr): 1710, 1595, 1550, 1490, 1430, 1405, 1262, 1212, 1164, 1100, 834, 744cm^{-1}. ^{1}H NMR($CDCl_3$): 3.73(2H, s), 7.46(4H, s). MS(m / z): 381(M^+–Cl, 28.7), 344(M^+–2Cl, 13.9), 318(13.7), 311(3.0), 172(base). Anal. calcd. for $C_{14}H_6Cl_6O_2$: C 40.14, H 1.44. Found: C 39.73, H 1.42.

Irradiation of CA with **7**: A solution of CA (0.500g, 2.03mmol) and **7** (0.400g,3.4mmol) in benzene (100ml) was photolysed for 6h. Solvent was evaperated *in vacuo*,the residue was washed with ethyl ether to give **16** (308mg, 50%) as solid product. The ether solution was concentrated and the residue was subjected to column chromatography on silica gel to give unreacted CA (78mg, a conversion of 84%) and TCH (90mg,21%).

16: M.p. 206–208℃. IR(KBr): 3050, 2970, 2900, 1668, 1600, 1565, 1280, 1265, 1120, 1102, 945, 762, 730cm^{-1}. ^{1}H NMR($CDCl_3$, 500MHz): 3.40(1H, dd, J = 18.1, 6.2Hz, 1 / 2 $C_\alpha H_2$), 3.58 (1H, d, J = 18.1 Hz, 1 / 2 $C_\alpha H_2$), 4.58 (1H, d, J = 6.2 Hz, H_γ), 5.91(1H, t, J = 6.2 Hz, H_β), 7.00–7.36(4H, m, Ar–H). MS(m / z): 324(M^+–HCl, 0.2), 244(2.4), 211(2.0). 116(base). Anal. calcd. for $C_{15}H_8Cl_4O_2$: C 49.76, H 2.23. Found: C 49.26, H 2.14.

Irradiation of CA with **8**: A solution of CA (1.00g, 4.1mmol) and **8** (1.48g, 8.1mmol) in benzene (100ml) was photolysed for 5.5h to afford **17**(1.40g,80%) and an unidentified product (31mg, 1.7%).

17: M.p. 166–167℃. IR(KBr): 1682, 1609, 1576, 1497, 1443, 1271, 1105, 992, 938, 905, 826, 733, 673cm^{-1}. ^{1}H NMR ($CDCl_3$): 5.38 (1H, d, J = 6Hz), 7.26 (1H, d, J = 6Hz), 6.70–7.50(5H, m). MS (m / z): 348(M^+–79, 18.8), 319(60.2), 283(29.4), 182(85.9), 103(base). Anal. calcd. for $C_{14}H_7BrCl_4O_2$: C 39.20, H 1.65. Found: C 39.41, H 1.66.

Irradiation of CA with **9**:

In benzene: A solution of CA (1.00g, 4.1mmol)and **9**(2.00g, 24mmol) in benzene (100ml) was photolysed for 5h to give recovered CA (0.118g, a conversion of 88%), **18**(0.295g, 20%) and TCH (0.370g, 42%).

18: M.p. 212–214℃. IR(KBr): 2920, 2850, 1720, 1450, 1115, 1020, 890, 805, 740, 675cm^{-1}. $_1$H NMR(CDCl$_3$): 1.36(8H, br, 4CH$_2$), 1.71(8H, br, 4CH$_2$), 2.67(2H, br, 2CH). 3.21(2H, br, 2CH). MS(m / z): 373(M$^+$–Cl, 9.5), 338(14.6), 337(23.9), 303(14.7), 81(base). Anal. calcd. for $C_{18}H_{20}Cl_4O_2$: C 52.71, H 4.91. Found: C 52.68, H 4.80.

In acetonitrile: A solution of CA (1.00g, 4.1mmol) and **9**(2.00g, 24mmol) in acetonitrile (100ml) was photolysed for 4.5h to give unreacted CA (0.089g, a conversion of 91%), **19**(0.487g, 40%) and TCH(0.423g, 46%).

19: M.p. 105–107℃. IR(KBr): 3400, 3005, 2920, 2810, 1650, 1548, 1435, 1388, 1202, 1000, 945, 710cm^{-1}. ^{1}H NMR(CDCl$_3$): 2.05(6H, m, 3CH$_2$), 4.70(1H,m,CH), 6.31(3H, m, CH=CH, OH). MS(m / z): 292(1.0), 250(8.5), 248(17.9), 244(1.7), 211(2.1), 81(base). Anal. calcd. for $C_{12}H_{10}Cl_4O_2$: C 43.94, H 3.07. Found: C 44.07, H 2.95.

In dichloromethane: A solution of CA (1.00g, 4.1mmol) and **9** (2.00g, 24mmol) in dichloromethane (100ml) was photolysed for 3.5h to give unreacted CA (26mg, a conversion of 97%), **18**(0.326g, 20%), **19**(0.560g, 43%) and TCH (0.150g, 16%).

Formation Constant for CTC of CA with 7. The UV–visible spectroscopic measurements were done with a pair of matched quartz cells. To a solution of CA (1.003×10^{-3}M) in CCl$_4$, the donor (**7**) was added stepwise to a large excess. The spectrum of the solutions was recorded. Benesi–Hildebrand treatment[30] was employed to calculate the extinction coefficient ε_{CT} and the formation constant K_{CT} of the complex. The plot of 1 / 〔7〕 ~ 〔CA〕 / A_{CT} gave a straight line with correlation coefficient r=0.999. The ε_{CT} is 888 M^{-1}cm^{-1} (467nm) and K_{CT} is 1.1 M^{-1} as calculated from the intercept and the slope respectively. The saturation fraction used in this measurement is in the range of 0.37~0.63 (S=K_{CT} 〔7〕 / (1+K_{CT} 〔7〕)[54]. Treatment of the data with Scott[55] and Scatchard[55] methods gave ε_{CT} and K_{CT} values with errors not exceeding ± 10% from that by Benesi–Hildebrand method.

Acknowledgement: this work was supported by the National Natural Science Foundation of China.

References

1. Bruce, J. M. *Photochemistry of Quinones*, in *The Chemistry of Quinoid Compounds*, Part 1, ed. Patai, S. Wiley, New York, 1974.
2. Maruyama, K. *Recent Advances in the Photochemistry of Quinones*, in *The Chemistry of Quinoid Compounds*, Part 2, ed. Patai, S; Rappoport, Z. Wiley, New York, 1988.
3. Bryce–Smith, D.; Gilbert, A.; Johnson, M. G. *J.Chem. Soc. C*, **1967**,383.
4. Bunce, N. J.; Hadley, M.*Can. J. Chem.* **1975**, *53*,3240.
5. Bunce, N. J.; Ridley, J. E.; Zerner, M. C. *Theoret. Chim. Acta(Berl.)***1977**,*45*, 283.
6. Wilson, R. M.; Wunderley, S. W.; Walsh, T. F.; Musser, A. K.; Outcalt, R.; Geiser, F.; Gee, S. K.; Brabender, W.; Yerino, L.; Conrad, T.T.; Tharp, G.A. *J.Amer.Chem.Soc.*

1982,*104*,4429.

7. Bryce–Smith, D.; Evans, E.H.; Gilbert, A.; NcNeill,H.M. *J.Chem. Soc., Perkin 2,* **1991**, 1587.
8. Barltrop, J.A.; Hesp,B. *J.Chem. Soc.C,* **1967**, 1625.
9. Maruyama, K.; Naruta,Y; Otsuki,T. *Bull.Chem. Soc. Jpn.***1975**, *48*,1553.
10. Mori, A.; Takeshita,H. *Bull.Chem.Soc.Jpn.***1985**, *58,* 1581.
11. Bryce–Smith,D.; Gilbert,A.; Evans,E.H.; McNeill,H.S. *J.Chem.Soc.,Perkin 1*,**1991**,485.
12. Maruyama,K.; Otsuki,T.; Tai,S. *J.Org.Chem.***1985**, *50,* 52.
13. Maruyama,K.;Tai,S. *Chem.Lett.* **1985**,681.
14. Maruyama,K.; Imahori,H. *Bull.Chem.Soc.Jpn.***1989**, *62,* 816.
15. Maruyama,K.; Imahori,H. *J.Org.Chem.***1989**,*84,* 2693.
16. Maruyama,K.; Imahori,H. *J.Chem.Soc., Perkin* 2,**1990**, 257.
17. Schenk,G.O. Z.*Electrochem.*,**1960**,*64*,997.
18. Bryce–Smith,D.; Gilbert,A. *Tetrahedron Letters,* **1964**, 3471.
19. Miyashi,T.; Konno,A.; Takahashi,Y.; Kaneko,A.; Suzuki,T.; Mukai,T. *Tetrahedron Letters*,**1989**,*30*,5297.
20. Christl,V.M.; Braun,M. *Angew.Chem.***1989**,*101*,636.
21. Guerry–Butty,E.; Haselbach,E.; Pasquier,C.; Suppan,P.*Helv.Chim.Acta*,**1985**,*68,* 912.
22. Hilinski,E.F.; Milton,S.V.; Rentzepis,P.M.*J.Amer.Chem.Soc.***1983**, *105*,5193.
23. Peover,M.E. *Nature (London)*,**1961**,*191*,702.
24. Foster, R. *Organic Charge Transfer Complexes,* Academic, New York, 1969.
25. Andrews, L.J.; Keefer, R.M. *J. Org. Chem.* **1988**, *53,* 537.
26. Andrews, L.J.; Keefer, R.M. *J. Org. Chem.* **1988**, *53,* 2163.
27. Brunn, V.J.; Peters, F.; Dethloff, M. *J. Prakt. Chemie,* **1976**, *318,* 745.
28. Fukuzumi, S.; Kochi, J.K. *J.Org.Chem., 1981, 46,* 4116.
29. Turchaninov, V.K.; Petrushenko, K.B.; Vokin, A.I.; Ermikov, A.F.; Eskova, L.A.; Baikalova, L.V.; Domnina, E.S. *Zh. Org. Khim.*, **1989**, *25,* 1138.
30. Benesi, H.A.; Hildebrand, J.H. *J.Amer. Chem. Soc.*, **1949**, *71,* 2703.
31. Yamada,H.; Saheki,M.; Fukushima,S.; Nagasao,T.*Spectrochimica Acta*,**1974**, *30A,* 295.
32. Weller,A.*Z.Phys.Chem.(Wiesbaden).* **1982**, *133,* 193.
33. Gschwind,R.; Haselback,E. *Helv.Chim.Acta*,**1979**, *62,* 941.
34. Miller,L.L.; Nordblom,G.D.; Mayeda,E.A.*J.Org.Chem.* **1972**, *37*,916.
35. Trofimov, B.A.; Molder, U.; Pikver, R.; Vyalykh, E.P.; Nedolya, N.A., *Izv. Akad. Naud SSSR,Ser.Khim.* **1974**, 2731(Russ.).
36. Yilmaz,H.; Yurtsever,E.; Toppare,L. *J.Electrochem. Interfacial Electrochem.* **1989**, *261,* 105.
37. Larson,R.C.; Iwamoto,R.T.;Adams,R.N.*Anal.Chim.Acta*,**1961**, *25,* 371.
38. Traylor,T.G.; Xu,F.*J,Amer,Chem,Soc*,**1988**, *110,* 1953.
39. Toppare,L.; Eren,S.; Akbulut,O. *J.Polym.Sci.,polym.Chem.Ed.***1985**, *23,* 303.
40. Rentzepis,P.M.; Steyert,D.W.; Roth,H.D.; Albert,C.J. *J.Phys.Chem.***1985**, *89,* 3955.
41. Masnovi, J.M.; Kochi, J.K.; Hilinski, E.F.; Rentzepis, P.M. *J. Amer. Chem. Soc.* **1986**,

108, 1126.

42. Kobashi, H.; Funabashi, M.; Kondo, T;Morita, T.; Okada, T.; Mataga, N. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3557.
43. Maslak, P.; Chapman, Jr., W.M., *J.Chem. Soc., Chem. Commun.* **1989**, 1809.
44. Jones, G., II ; Haney, W.A.; Phan, X.T. *J. Amer. Chem. Soc.*, **1988**, *110*, 1922.
45. Pac,C.; Nakason,A.; Sakurai,H.*J.Amer.Chem.Soc.***1977**, *99*,5806.
46. Majima,J.; Pac,C.; Nakason,A.; Sakurai,H.*J.Amer.Chem.Soc.***1981**,*103*,4499.
47. Albert,C.J.; Roth,H.D.; Schilling,M.L.M. *J.Amer.Chem.Soc.***1985**, *107*, 4148.
48. Mattes,S.L.; Farid,S.*J.Amer.Chem.Soc.***1986**, *108*,7356.
49. Lopez,L.; Calo,V.; Aurora,R. *J.Photochem.* **1986**, *32*,95.
50. Meites,L.; Zuman,P.; *CRC Handbook Series of Organic Electrochemistry*, Vol.1, CRC press, Cleveland, 1977.
51. Creed,D.; Caldwell,R.A.*J.Amer,Chem.Soc.* **1974**, *96*,7369.
52. Coyle,J.D. *Chem.Rev.***1978**, *78*, 97.
53. Jung, M.E.; Light, L.A. *J.Org.Chem.* **1982** *47*, 1089.
54. Deranleau, D.*J.Amer.Chem.Soc.*, **1969**, *91*, 4044.
55. Foster, R. *Molecular Complexes*, Vol.2, Elok Science, London, 1974.

(*Received in China* 14 *April* 1993; *accepted* 19 *October* 1993)