CHEMISTRY LETTERS, pp. 1451-1454, 1993.

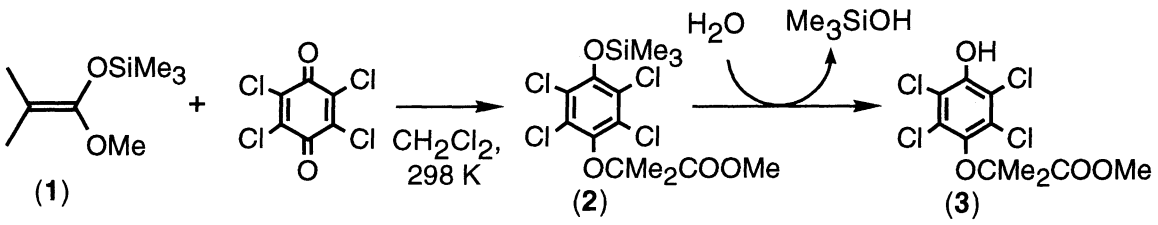
Electron Transfer *vs.* Nucleophilic Addition of Ketene Silyl Acetals with Halogenated *p*-Benzoquinone Derivatives

Shunichi FUKUZUMI,* Morifumi FUJITA, Gen-etsu MATSUBAYASHI,*† and Junzo OTERA*††
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565
†Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560
††Department of Applied Chemistry, Okayama University of Science, Ridai-cho, Okayama 700

A β,β-dimethyl-substituted ketene silyl acetal reduces *p*-chloranil to produce the carbon-oxygen adduct, the hydrolysis of which yields the corresponding hydro-quinone ether (**3**). The structure of **3** has been determined by the X-ray crystal analysis. On the other hand, the reaction of a nonsubstituted ketene silyl acetal with *p*-fluoranil yields the carbon-carbon adduct selectively. The mechanistic difference between the C-O and C-C bond formation is elucidated based on the kinetic study.

We have recently reported that β-methyl-substitution of ketene silyl acetals increases the electron-donor ability to be becoming more susceptible to the electron-transfer oxidation, although it generally increases the steric hindrance of the reaction center, thereby reducing the reactivity of the nucleophilic attack toward electrophiles.[1,2] Extension of these two reverse effects leads us to expect the mechanistic change from ubiquitous S_N2 processes to novel electron-transfer pathways. Such electron transfer *vs.* nucleophilic alternative has been one of the central proposition in reaction mechanism.[3] Moreover, the electron-transfer oxidation of ketene silyl acetals and enol silyl ethers has been receiving increased attention recently because of its synthetic utility.[4] In this context, an electron-transfer mechanism has recently been reported for the reduction of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), which is known as a strong organic one-electron oxidant, by silyl enol ethers, although a nucleophilic attack of the silyl enol ether on DDQ cannot be ruled out.[5] This study reports that the electron transfer or nucleophilic pathway is changed drastically depending on the β-methyl-substitution of ketene silyl acetals in the addition reactions with relatively mild oxidants as compared to DDQ, *i.e.*, halogenated *p*-benzoquinone derivatives to yield different products, carbon-oxygen and carbon-carbon adducts, respectively.[6]

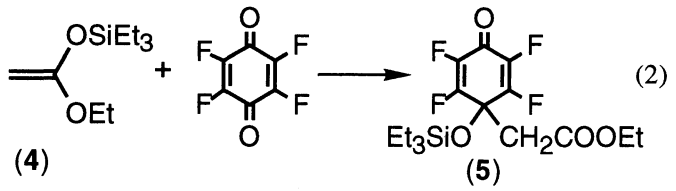
p-Chloranil is readily reduced by a β,β-dimethyl-substituted ketene silyl acetal (**1**) to yield the carbon-oxygen adduct (**2**), the hydrolysis of which yields the corresponding hydroquinone ether (**3**), Eq. 1. The



(1)

carbon-oxygen bond formation has been confirmed by the X-ray crystal analysis of **3** (Fig. 1).[7] The carbon-

oxygen adducts are also obtained by the reactions of **1** with other halogenated *p*-benzoquinone derivatives, *p*-bromanil, *p*-fluoranil, and dichloro-*p*-benzoquinone. In contrast, the reaction of a nonsubstituted ketene silyl acetal (**4**) with *p*-fluoranil yields selectively the carbon-carbon adduct (**5**), which is identified by the ^{1}H, ^{13}C, and ^{19}F NMR spectra (Eq. 2).[8]



(2)

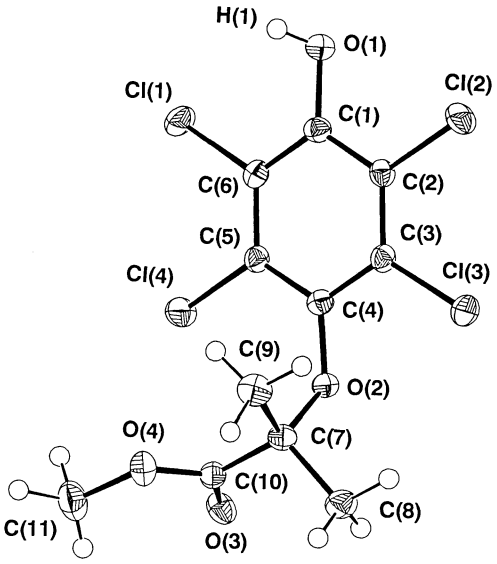


Fig. 1. ORTEP drawing of **3**.

Rates of the reactions of *p*-benzoquinone derivatives with large excess amounts of ketene silyl acetals were followed by the disappearance of the absorbance due to *p*-benzoquinone derivatives, obeying the ordinary pseudo-first-order kinetics. The pseudo-first-order rate constant (k_f) increases linearly with an increase in the concentration of ketene silyl acetal [**1**] at the low concentrations but exhibits a curvature from the linear dependence at the high concentration region. Such a curved dependence of k_f on [**1**] is consistent with the independent, spectroscopic evidence for the formation of charge-transfer (CT) complexes in benzene, which must be accommodated in any mechanistic formulation for the addition of ketene silyl acetal to *p*-benzoquinone derivatives. If the CT complex is a precursor for the reduction of *p*-chloranil by **1**, the dependence of k_f on [**1**] may be expressed by Eq. 3, in which k_1 is the first-order rate constant for the reaction through the CT complex and K_{CT} is the formation constant of the CT complex. Equation 3 is rewritten by Eq. 4, which predicts a linear correlation between k_f^{-1} and $[\mathbf{1}]^{-1}$. In fact, the plots of k_f^{-1} *vs.* $[\mathbf{1}]^{-1}$ for the

$$k_f = k_1K_{CT}[\mathbf{1}] / (1 + K_{CT}[\mathbf{1}]) \quad (3) \qquad k_f^{-1} = k_1^{-1}[1 + (K_{CT}[\mathbf{1}])^{-1}] \quad (4)$$

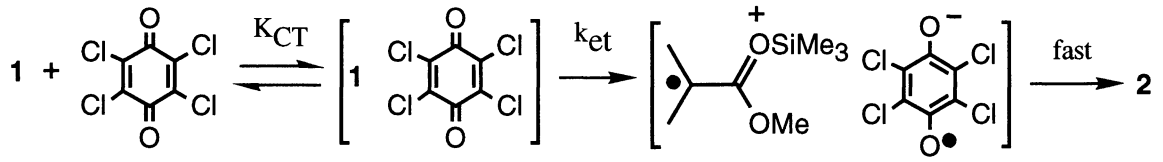
reactions of **1** with *p*-chloranil and other *p*-benzoquinone derivatives gave the linear correlation. From the intercepts and slopes are obtained the k_1 and K_{CT} values which are listed in Table 1 together with the one-electron reduction potentials (E^0_{red}) of quinones[9] and the CT absorption maxima (λ_{CT}). The observed second-order rate constant ($k_{obsd} = k_1K_{CT}$) generally decreases with a decrease in the one-electron reduction potential (E^0_{red}) of quinones. As such the highest reactivity is achieved for *o*-chloranil (E^0_{red} = 0.14 V), but no reaction takes place for chloro-*p*-benzoquinone (E^0_{red} = -0.34 V) and *p*-benzoquinone (E^0_{red} = -0.50 V). Such a strong dependence of k_{obsd} on E^0_{red} indicates that electron transfer from **1** to quinones may be the rate-determining step for addition of **1** to quinones as shown representatively for the **1**-*p*-chloranil system in Scheme 1. The rate constant of intracomplex electron-transfer in the CT complex may be evaluated based on the Rehm-Weller Gibbs energy relation for electron-transfer processes in Eq. 5,[1,10] where ΔG^0_{et} is the Gibbs energy change of electron transfer in the CT complex and $\Delta G^{\neq}_0$ is the intrinsic barrier of the electron-transfer reactions of **1**. The

$$\Delta G^{\neq}_{et} = (\Delta G^0_{et}/2) + [(\Delta G^{\neq}_0)^2 + (\Delta G^0_{et}/2)^2]^{1/2} \quad (5)$$

Table 1. Rate Constants for the Addition Reactions of **1** and **4** with *p*-Benzoquinone Derivatives in CH_2Cl_2 at 298 K, the Absorption Maxima (λ_{CT}) of the CT Bands of Complexes of **1** with *p*-Benzoquinone Derivatives in Benzene, and the One-Electron Reduction Potentials (E^0_{red}) of *p*-Benzoquinone Derivatives in MeCN at 298 K

Benzoquinone	E^0_{red} V *vs.* SCE	λ_{CT} nm	k_{obsd}[a] $dm^3\ mol^{-1}\ s^{-1}$	k_1 s^{-1}
o-Chloranil	0.14	b)	5.4×10^2	b)
p-Fluoranil	-0.04	495	4.4×10^{-1} (5.8)	4.0×10^{-1}
p-Chloranil	0.01	510	3.5×10^{-2} (2.6×10^{-2})	4.4×10^{-2}
p-Bromanil	0.00	500	7.4×10^{-3} (1.2×10^{-2})	1.4×10^{-2}
2,6-Dichloro-*p*-benzoquinone	-0.18	477	1.0×10^{-2}	1.4×10^{-2}
2,5-Dichloro-*p*-benzoquinone	-0.18	472	1.9×10^{-3}	c)
Chloro-*p*-benzoquinone	-0.34	440	d)	d)
p-Benzoquinone	-0.50	e)	d)	d)

a) The values in parentheses are those for the reactions of **4**. b) The reaction was too fast to determine the value accurately. c) Not determined. d) No reaction or the rate was too slow to be determined accurately. e) Not determined because of the overlap with the absorption band of *p*-benzoquinone.



Scheme 1.

ΔG^0_{et} value may be given by Eq. 6, where the E^0_{ox} value of **1** (0.90 V)[1] and the E^0_{red} values of quinones

$$\Delta G^0_{et} = F(E^0_{ox} - E^0_{red}) + w_p \quad (6)$$

(Table 1)[9] are known, and w_p is the work term which is required to bring the radical cation of **1** and the quinone radical anion to the mean separation distance of the transition state. The w_p value for such a radical ion pair with opposite charge may be evaluated as ca. 0.1 eV although the w_p value is sensitive to the steric effect.[11] The $\Delta G^{\neq}_0$ value of **1** has previously been reported as 5.2 kcal mol^{-1}.[1] By using these values the $\Delta G^{\neq}_{et}$ value can be evaluated as 19.6 kcal mol^{-1} for the **1**-*p*-chloranil system, which is converted to the rate constant of intracomplex electron transfer (k_{et}) by $k_{et} = (kT/h) \exp(-\Delta G^{\neq}_{et}/RT)$. The k_{et} value thus evaluated is 2.7×10^{-2} s^{-1} which agrees well with the observed k_1 value (4.4×10^{-2} s^{-1}) in Table 1. Such agreement supports strongly the electron-transfer pathway in Scheme 1, since no significant interaction is required for the electron-transfer process as compared to an alternative nucleophilic process.

The reactivities of a nonsubstituted ketene silyl acetal (**4**) towards *p*-fluoranil, *p*-chloranil, and *p*-bromanil are compared in Table 1 (the values in parentheses). The one-electron oxidation potential of **4** (1.30 V) is significantly higher than that of **1** (0.90 V).[1] Thus, the reactivity of **4** would be reduced by 10^8 times as

compared to **1** based on Eq. 5. However, the k_{obsd} values of **4** are even much larger than those of **1** except for the case of *p*-chloranil. In such a case the nucleophilic attack of **4**, which is less sterically hindered than **1**, may dominate as compared to the electron-transfer pathway, yielding the carbon-carbon adduct (Eq. 2). The 1,2-addition may take place in a concerted manner, which may be energetically more favorable than alternative electron-transfer pathway. Such a concerted nucleophilic process is retarded in the case of the sterically hindered ketene silyl acetal (**1**), which can in turn transfer an electron to *p*-benzoquinone derivatives to yield the carbon-oxygen adduct (Scheme 1). Thus, the β,β-dimethyl-substitution of ketene silyl acetals results in the drastic mechanistic change from ubiquitous S_N2 processes to a novel electron-transfer pathway.

References

1) S. Fukuzumi, M. Fujita, J. Otera, and Y. Fujita, *J. Am. Chem. Soc.*, **114**, 10271 (1992).

2) T. Sato, Y. Wakabayashi, J. Otera, H. Nozaki, and S. Fukuzumi, *J. Am. Chem. Soc.*, **113**, 4028 (1991); J. Otera, Y. Fujita, T. Sato, H. Nozaki, S. Fukuzumi, and M. Fujita, *J. Org. Chem.*, **57**, 5054 (1992).

3) J.-M. Mattalia, B. Vacher, A. Samat, and M. Chanon, *J. Am. Chem. Soc.*, **114**, 4111 (1992) and references cited therein.

4) M. T. Reetz, K. Schwellnus, F. Hübner, W. Massa, and R. E. Schmidt, *Chem. Ber.*, **116**, 3708 (1983); G. E. Totten, G. Wenke, and Y. E. Rhodes, *Synth. Commun.*, **15**, 291 (1985); R. Rothore, Z. Lin, and J. K. Kochi, *Tetrahedron Lett.*, **34**, 1859 (1993).

5) A. Bhattacharya, L. M. DiMichele, U.-H. Dolling, E. J. J. Grabowski, and V. J. Grenda, *J. Org. Chem.*, **54**, 6118 (1989). An efficient method for the conversion of ketones to enones *via* the reaction of enol silyl ethers with DDQ has previously been reported: I. Ryu, S. Murai, Y. Hatayama, and N. Sonoda, *Tetrahedron Lett.*, **1978**, 3455.

6) The reduction of *p*-chloranil by cyclohexanone enol trimethylsilyl ether *via* photoinduced electron transfer has recently been reported as a communication: T. M. Bockman, S. Perrier, and J. K. Kochi, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 595.

7) The desilylated product **3** was isolated by the hydrolysis of **2** and then crystallized in CH_2Cl_2. Anal. Found: C, 37.66; H, 2.72%. Calcd for $C_{11}H_{10}Cl_4O_4$: C, 37.96; H, 2.90%. Crystal data for **3**: monoclinic, space group $P2_1/c$, a = 15.826 (2), b = 10.3295(9), c = 8.794(5) Å, β = 101.23(2)°, V = 1410.1(9) Å^3, Z = 4, D_c = 1.639(1) g cm^{-3}, D_m (floating) = 1.63 g cm^{-3}, and μ(Cu - Kα) = 77.1 cm^{-1}. The structure was solved according to the direct (MULTAN) method and refined by the block-diagonal least-squares method. The final refinement converged at R = 0.039 and R' = 0.041 for 2130 reflections with $|F_o| > 3\sigma(F)$. **2**: ^{1}H NMR ($CDCl_3$) δ 0.33 (s, 9H), 1.58 (s, 6H), 3.84 (s, 3H).

8) **5**: ^{1}H NMR ($CDCl_3$) δ 0.61 (q, 6H, J = 7.8 Hz), 0.93 (t, 9H, J = 7.8 Hz), 1.20 (t, 3H, J = 7.3 Hz), 3.20 (s, 2H), 4.11 (q, 2H, J = 7.3 Hz); ^{13}C NMR ($CDCl_3$) δ 5.47, 6.40, 13.94, 40.62, 61.50, 70.66 (t, J_{CF} = 24 Hz), 137.93 (dt, J_{CF} = 267, 7 Hz), 153.49 (dt, J_{CF} = 283, 10 Hz), 166.69, 172.06 (t, J_{CF} = 22 Hz); ^{19}F NMR ($CDCl_3$) δ($CFCl_3$) 132,54 (d, J_{FF} = 11 Hz), 157.65 (d, J_{FF} = 11 Hz).

9) D. H. Evans, "Encyclopedia of Electrochemistry of the Elements, Organic Section," ed by A. J. Bard and H. Lund, Marcel Dekker, New York (1978), Chapter XII-1.

10) A. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).

11) S. Fukuzumi, K. Hironaka, N. Nishizawa, and T. Tanaka, *Bull. Chem. Soc. Jpn.*, **56**, 2220 (1983).

(Received May 10, 1993)