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Chemical Reaction Following Electroreduction of Benzophenones. 2. Relationship between the Rate Constant of Disproportionation and Spin Density

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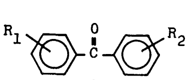
Synopsis. Electroreduction of benzophenones in DMF in the presence of Li^+ was investigated by cyclic voltammetry. Most of these radical anions underwent disproportionation reactions. The relationship between the logarithm of the rate constant of the reaction and the spin density of the carbon atom at the carbonyl group was found to be linear.

In recent years there have been numerous investigations dealing with the behavior of radical anions generated in various ways.[1-3] Generally the radical anions undergo a dimerization[4,5] or a disproportionation reaction[6] in the presence of cations.

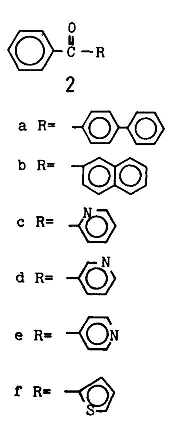
The authors reported in the previous paper[7] that the disproportionation of the electrogenerated radical anions of several substituted benzophenones **1** were accelerated by the addition of lithium iodide, and that a linear relationship was found between the logarithms of the rate constants of the disproportionation, ln k_{obsd}, evaluated from cyclic voltammetry (CV). This was confirmed by the digital simulation and the spin density, ρ_{s}, of the carbon atom at the carbonyl group of benzophenones. In this paper, we report that the above relationship is valid for the other benzophenones, **2** and **3**. Furthermore, a linear relationship between ln k_{obsd} and the electron density, q, of the oxygen atom at the carbonyl group was found for benzophenones **1**, **2**, and **3**.

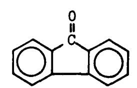


1

a R_1=H, R_2=H
b R_1=*o*-CH_3, R_2=H
c R_1=*m*-CH_3, R_2=H
d R_1=*p*-CH_3, R_2=H
e R_1=*p*-CH_3, R_2=*p′*-CH_3
f R_1=*p*-OCH_3, R_2=H
g R_1=*p*-OCH_3, R_2=*p′*-OCH_3

2





3

Experimental

Chemicals. All the substituted benzophenones (**1a**, **1d**, **1e**, **2c**, **2d**, **2e**: Waco, **1b**, **1c**, **2a**: Aldrich, **1f**, **1g**, **2b**, **2f**, **3**: Tokyo Kasei) were purified by recrystallization. Benzyl alcohols used as authentic samples for a high performances liquid chromatography (HPLC) were prepared with the method of Meerwein-Pondorf: α-(4-biphenyl)benzyl alcohol **4**: mp 97.0—97.5 °C (lit,[8] 96 °C), IR(KBr) 3260 cm^{-1} (OH); α-(2-thienyl)benzyl alcohol **5**: mp 56.5 °C (lit,[9] 57—58 °C); IR (KBr) 3260 cm^{-1} (OH), α-(*p*-methoxyphenyl)benzyl alcohol **6**: mp 66—67 °C (lit,[10] 59—60 °C), IR (KBr) 3270 cm^{-1} (OH).

CV. CV was carried out in the same way as described in the previous paper.[7] The differecne between cathodic peak and the switching potentials was 0.1V. The sweep rate was 0.1V/s.

Controlled Potential Electrolysis. Reduction of 2.0 g of **2a** in 100 ml of DMF containing 3.0 g of LiI was carried out at the potential of the first wave, −1.80 V *vs.* SCE. After passing 2*F*** of electricity, the catholyte was analyzed by HPLC.

Results and Discussion

The first wave of the voltammogram for **2a** is a reversible one-electron transfer: $i_{\mathrm{pa}}/i_{\mathrm{pc}}=1$ and $|E_{\mathrm{pc}}-E_{\mathrm{pa}}|=70$ mV. By the addition of LiI, i_{pa} decreases and i_{pc} increases slightly. Controlled potential electrolysis at −1.80 V *vs.* SCE in the presence of Li^+ gave **4**, a two-electron reduction product in 70% yield. All the remainder except the product was the starting material. These results show that the following disproportionation occurs:

$$\mathrm{R} + \mathrm{e} \rightleftarrows \mathrm{R}^{\overline{\cdot}}$$
$$2\mathrm{R}^{\overline{\cdot}} \longrightarrow \mathrm{R}^{=} + \mathrm{R},$$

where R is a reactant, $\mathrm{R}^{\overline{\cdot}}$ a radical anion and $\mathrm{R}^{=}$ a dianion of a reactant.

The profile of the voltammogram for other benzophenones examined was similar to that of **2a**. The electrolysis of **2f** and **1f** gave **5** and **6** in 30% and 62% yield, respectively. In both cases, the remainder was mostly the starting material. From the above results we concluded that the following chemical reaction was disproportionation for all the benzophenones tested. The rate constants of disproportionation, k_{obsd}, were estimated from the voltammetric data of these compounds by using digital simulation (Table 1). The plots of ln k_{obsd} against ρ_{s} gave a straight line as shown in Fig. 1. It was confirmed that the k_{obsd} was predictable from the ρ_{s}.

The reaction rate of benzophenones having an electron-attracting substituent (**2a**, **2b**) and having a hetero atom (**2c**, **2d**) would tend to be slower than that of **1a**. **1b** and **3** exhibited reversible cyclic voltammograms even in the presence of 16-fold concentration excess of Li^+. This does not promote the reaction. The behavior of **1b** can be attributed to the 2-methyl group which inhibits mutual access to the carbon atom in the carbonyl group, and that of **3** to both steric hindrance (corresponding to the 2 and 2′ positions of

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** *F*=96487 C mol^{-1}.

Table 1. Experimental data and calculated parameter for benzophenones

Compd	$-E_{\mathrm{pc}}$[a] / V	$k_{\mathrm{obsd}}\times 10^{3}$ [a,b] / $\mathrm{M^{-1}\,s^{-1}}$	ρ_s[d]	q[e]	Ref.
1a	1.79	0.39	0.3437	1.7374	7
1b	1.85	—	0.3467	1.7465	7
1c	1.80	0.50	0.3462	1.7379	7
1d	1.83	0.70	0.3589	1.7486	7
1e	1.90	1.90	0.3810	1.7605	7
1f	1.86	3.89	0.3510	1.7446	7
1g	1.98	0.57[c]	0.3597	1.7518	7
2a	1.71	0.23	0.3111	1.7308	
2b	1.70	0.93	0.3121	1.7295	
2c	1.56	0.32	0.3294	1.7270	
2d	1.64	0.90[c]	0.3403	1.7363	
2e	1.48	0.21	0.3198	1.7242	
2f	1.65	0.62	0.3526	1.7554	
3	1.30	—	0.2827	1.6963	

a) Determined with a hanging mercury drop electrode. b) The rate constant of the disproportionation in the presence of 4 mM (1 M = 1 mol dm^{-3}) LiI. c) 0.4 mM LiI. d) Calcd by employing McLachlan's procedure; $\lambda = 1.2$. e) Calcd by employing the Hückel MO theory.

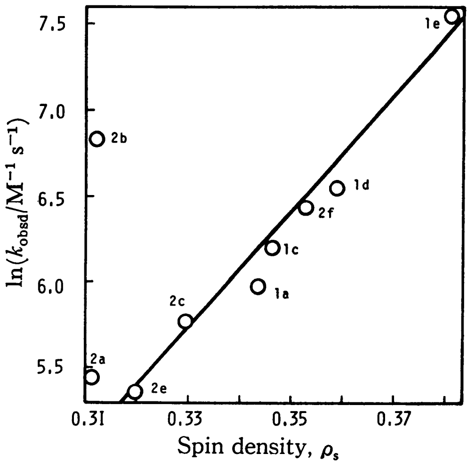

Fig. 1. Correlation between the rate constant of the disproportionation, k_{obsd}, and the spin density, ρ_s, for benzophenones.

1a) and the lowering of ρ_s.

Furthermore the plots of ln k_{obsd} against q were found to be linear. This suggested that ρ_s and q may bear a linear relationship to each other. Thus, the change in k_{obsd} with ρ_s and/or q is probably based on the change in association constants for the ion-pair formation between radical anions and Li$^+$. At present, unfortunately, no association constants of the ion-pairs have been obtained; and the contribution of ρ_s and q to k_{obsd} cannot be discussed separately.

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