October, 1980] © 1980 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 53, 3015—3016 (1980) 3015

Relative Electron-capture Efficiency of Disubstituted Benzene in γ-Irradiated MTHF Glass at 77 K

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(Received December 28, 1979)

Synopsis. The relative electron-capture efficiencies of disubstituted benzenes were measured by a competitive method. It was found that the efficiencies of the disubstituted benzenes are correlated with the reactivity towards nucleophilic species as expressed by Hammett's substituent constant. The logarithmic values of the efficiency are roughly proportional to the polarographic half-wave reduction potentials and to the electron affinities.

A number of investigations aimed at determining the rate constant of the electrons ejected by the irradiation of ionizing radiation with various compounds in aqueous and organic solutions have been performed by the competitive-reaction or pulse-radiolysis technique. In a previous paper,[1] a study was made of electron-capture reactions by polychlorinated benzenes and halogenated benzenes in MTHF glass at 77 K by a competitive method, and the relationship between the reactivity and the electron affinity of these molecules was discussed.

In this paper, the electron-capture efficiencies of many disubstituted benzenes relative to that of biphenyl will be determined in the MTHF glass, and the effects of the substituents on the efficiency will be described.

Experimental

The disubstituted benzenes, except for *p*-chlorobenzonitrile (an Eastman reagent chemical), were of a guaranteed grade and were obtained from the Tokyo Kasei Kogyo Co., Ltd. These chemicals were used without further purification. The measurement of the relative electron-capture efficiency was carried out by the competitive method, biphenyl being used as the reference material (0.04 M).[1,2] The sample preparation, γ-irradiation, and other experimental conditions were described in a previous paper.[1] (1 M=1 mol/dm^3)

Results and Discussion

The relative electron-capture efficiency, K_s/K_{ϕ_2}, and the ratio to the parent compound, K/K_0, are summarized in Table 1.

In a chlorobenzene series, the substituents, NO_2, $COCH_3$, and CN, markedly increased the efficiency for electrons. This result is consistent with the inductive effect of these substituents. The substitution of halogen atoms also increased the efficiency. The order of efficiency for halogen substituents was Br>Cl≫F.

On the other hand, all the electron-donating groups such as OH decreased the efficiency for electron-capture except for *p*-chlorotoluene. The decrease in the efficiency is generally in the order of $OH>OCH_3>CH_3$. This result is probably due to the resonance effect of the substituent on the ring.

In the other series, the effect of the substituent on the electron-capture efficiency is compatible with that obtained from the chlorobenzene series except for the nitrobenzene series. In the case of the nitrobenzene series, the secondary substituent scarcely changed the efficiency of the parent molecule at all.

TABLE 1. RELATIVE ELECTRON-CAPTURE EFFICIENCY AS DETERMINED BY THE COMPETITIVE METHOD

Compound	K_s/K_{ϕ_2}[a]	K/K_0[b]	$-E_{1/2}$[c]/V
Chlorobenzene	0.490	1	2.13
p-Nitro	12.2	24.9	1.08
p-Cyano	4.81	9.82	1.36
p-Acetyl	6.30	12.9	
p-Bromo	1.10	2.25	1.61
p-Chloro	1.03	2.10	1.81
m-Chloro	1.09	2.22	
p-Fluoro	0.569	1.16	
m-Fluoro	0.800	1.63	
p-Methyl	0.482	1.19	2.16
p-Methoxy	0.390	0.796	2.15
p-Hydroxy	0.270	0.551	
Bromobenzene	0.844	1	1.81
p-Iodo	2.73	3.24	1.08
p-Bromo	1.30	1.54	1.54
p-Chloro	1.10	1.30	1.61
p-Fluoro	0.840	0.995	
p-Methyl	0.735	0.871	1.84
p-Methoxy	0.667	0.790	1.84
p-Hydroxy	0.640	0.758	
Fluorobenzene	0.054	1	
p-Bromo	0.840	15.5	
p-Chloro	0.569	10.5	
p-Methyl	0.029	0.537	
Nitrobenzene	12.6	1	1.15
p-Chloro	12.2	0.968	1.08
p-Acetyl	12.8	1.02	
p-Methyl	11.8	0.936	
p-Methoxy	13.6	1.07	
Acetophenone	5.90	1	
p-Nitro	12.8	2.17	
p-Acetyl	10.9	1.85	
p-Bromo	7.20	1.22	
p-Chloro	6.30	1.07	
p-Methyl	5.82	0.986	
p-Methoxy	4.60	0.789	
p-Hydroxy	3.65	0.619	
Benzonitrile	2.40	1	2.17
p-Chloro	4.81	2.00	
p-Methyl	2.14	0.892	2.28
m-Methyl	3.10	1.29	2.22
p-Methoxy	1.30	0.542	

a) K_s/K_{ϕ_2}: Relative electron-capture efficiency (0.04 M biphenyl as reference). b) K/K_0: Ratio of the electron-capture coefficient for the parent molecule. c) Chlorobenzenes and bromobenzenes, Ref. 4; nitrobenzenes, Ref. 5; benzonitriles, Ref. 6.

In order to examine the substitution effects in detail, we attempted to determine whether or not the Hammett linear relation was applicable to the electron-capture reaction in MTHF glass. In Fig. 1, the log K/K_0 for a

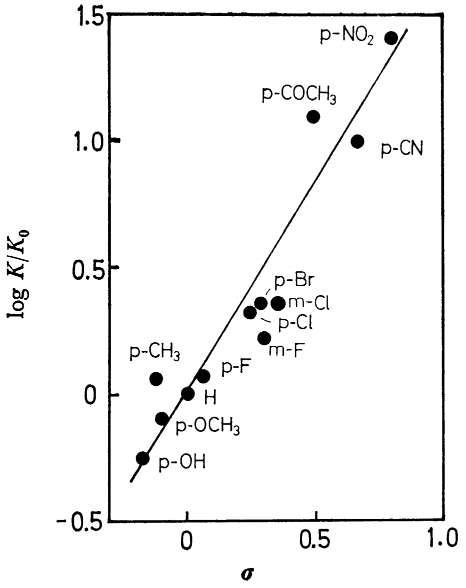

Fig. 1. Plot of log K/K_0 *vs.* Hammett substituent constant for a series of chlorobenzene.

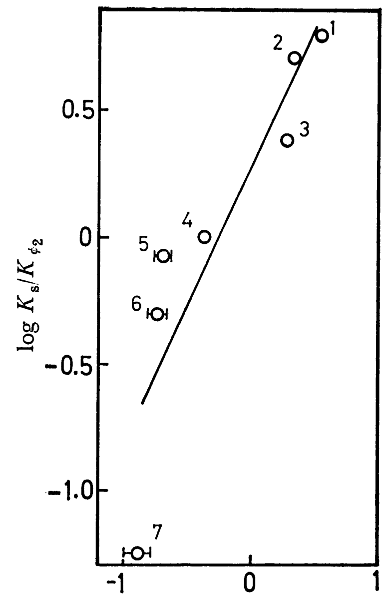

Fig. 2. Plot of log K_s/K_{ϕ_2} *vs.* the electron affinity for disubstituted benzenes.
1: p-$ClC_6H_4COCH_3$,[a] 2: $C_6H_5COCH_3$,[a] 3: C_6H_5CN,[a] 4: $C_{12}H_{10}$,[b] 5: C_6H_5Br,[c] 6: C_6H_5Cl,[c] 7: C_6H_5F.[c]
a) Thermal electron capture (Ref. 10). b) Theoretical (Ref. 11). c) Electron transmission spectroscopy (Ref. 12).

series of chlorobenzene is plotted as a function of the Hammett substituent constant (σ).[3] A linear correlation between the log K/K_0 and σ was observed, and the reaction constant, ρ, was obtained as 1.58 from the slope. The Hammett linear relation also conforms to the electron-capture reactions of the other series except for the nitrobenzene and benzonitrile series. For the acetophenone, bromobenzene, and fluorobenzene series, the ρ values obtained in the same way are 0.49, 0.52, and 3.12 respectively. One can find that the ρ value decreases with an increase in the electron-capture efficiency of the parent molecule in the order of acetophenone, bromobenzene, chlorobenzene, and fluorobenzene.

In a previous paper,[1] it was found that the log K_s/K_{ϕ_2} of polychlorinated benzene correlated well with the polarographic half-wave reduction potential ($E_{1/2}$). In the forth column in Table 1, the $E_{1/2}$ values are also listed.[4–6] A good correlation between the log K_s/K_{ϕ_2} and the $E_{1/2}$ is observed in the case of disubstituted benzenes.

Streitwieser confirmed that the $E_{1/2}$ was well correlated to the electron affinity, A, for many aromatic hydrocarbons.[7] Therefore, it is possible to replace $E_{1/2}$ by A, and the plot of log K_s/K_{ϕ_2} against A was found to be roughly linear (Fig. 2). This linear correlation suggests that the initial process of the electron-capture is related to the lowest unoccupied orbitals of the molecule (LUMO), since the A value corresponds to the energy of LUMO.[8]

The correlation in Fig. 2 can be expressed by the following empirical equation:

$$\log K_s/K_{\phi_2} = 1.10A + 0.04 \tag{1}$$

However, the slope of the line in Fig. 2 greatly deviates from a predictable slope for a diffusional process in the gas phase.[1] In the case of the glassy state at low temperatures, a treatment similar to that in the gas phase may be inapplicable, for Kira and Imamura indicated that the electron-tunneling process is important in MTHF glass at 77 K.[9]

Although the relative electron-capture efficiency does not directly correspond to the absolute rate constant, the relative magnitude of these values in Table 1 is a measure of the effects of the substituent on the parent molecule. The present results, however, do not provide sufficient data for discussing the nature of the electron-capture process in organic glasses.

The author is grateful to Dr. Takeshi Sawai for his valuable discussion.

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