February, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (2), 277—280 (1979) 277

# Correlation between Electron Capture Response and Chemical Structure for Benzyl Chlorides

Tsugio Kojima,* Masaru Satouchi,† and Yasukazu Tanaka
*Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606*
†*Department of Industrial Chemistry, Shiga Prefectural Junior College, Hikone, Shiga 522*

(Received March 6, 1978)

In the dissociative electron capture reaction of benzyl chlorides, all the substituents in the para position except for *t*-butyl group tend to decrease the activation energy, those in the meta position having no influence on the activation energy. This can be explained in terms of the contribution of a para substituent to the stabilization of the incipient radical in the transition state resulting from the delocalization of the odd electron. The resonance effect of the para substituent was compared with that obtained in the phenylation of substituted benzenes with phenyl radical, where phenylcyclohexadienyl radical is formed as an intermediate. The resonance effects in these two reactions agree, supporting the reaction mechanism proposed.

The principle of electron capture detection is based on the electron attachment to a molecule. Since an electron capture detector (ECD) gives data concerning only the probability of electron attachment to a molecule, the information obtained is not useful. However, if the temperature dependence of the electron capture coefficient is measured and analyzed, we can obtain useful information on the chemical structure of the molecule.[1–3)]

Wentworth and coworkers studied the electron attachment phenomenon on kinetics using the steady-state approximation, giving the electron capture response to the concentration of a capturing species in terms of electron capture coefficient $K$.[4–6)] According to Wentworth's theory, the molecular electron affinity or activation energy for an electron attachment accompanying a bond dissociation is obtained from $K$.

We proposed that the dissociative electron capture reaction of alkyl and aryl halides proceeds by a mechanism similar to that of $S_N2$ reaction.[1–2)] In the case of alkyl halides the magnitude of the activation energy is determined by the stability of the transition state, which depends upon the extent to which the odd electron on the α-carbon atom is delocalized by resonance. Although reports have appeared on the relative electron attachment coefficients for different organic compounds, little is known about the electron capture reaction in view of nucleophilic reaction. It is interesting to test this reaction model with various classes of compounds.

In the present paper, the results of measurements of activation energy in the electron capture reaction of benzyl chlorides are given, the substituent effect on the activation energy being discussed in terms of the reaction mechanism proposed for alkyl halides.[1)]

## Experimental

A modified Shimadzu GC-2C model gas chromatograph was used. The ECD employed was of a concentric type with 15 mCi nickel-63 as radioactive source. Applied voltage was supplied as a pulse through a pulse generator with an amplitude of 28 V, a pulse period of 3200 μs, and a pulse width of 3.2 μs; the electron capture reaction proceeded under field free conditions.

Glass columns (0.4 cm × 100 cm and 0.4 cm × 40 cm) were packed with Durapak (Carbowax 400/Porasil C), temperature being maintained at 70 or 100 °C. Nitrogen was used as a carrier gas. The oxygen in the carrier gas was removed by passing the gas through a tube packed with copper(I) chromate pellets. Another tube packed with Molecular Sieve 5A was used for the removal of moisture. The tubes were inserted between the cylinder of the carrier gas and the GC inlet.

Reagents except for commercial ones were synthesized. *m*-Methoxybenzyl chloride and *p*-*t*-butylbenzyl chloride: *m*-Methoxy- and *p*-*t*-butylbenzoic acids were reduced to the corresponding benzyl alcohols with lithium aluminum hydride in ether solution. They were converted into benzyl chlorides by chlorination with concd hydrochloric acid at 80 °C for 2 h. Alkylbenzyl chlorides were synthesized by the chlorination of alkyltoluenes with chlorine gas or sulfinyl chloride.

The compounds synthesized were identified by GC-MS technique. The sample solution was prepared by dilution with benzene to a concentration such that the detector current decreases to about a half of the back ground current.

The electron capture coefficient $K$ was calculated by the following equation derived by Wentworth and Chen:[5)]

$$\frac{F}{S}\int\frac{(I_b-I_e)}{I_e}\mathrm{d}x = Kn, \tag{1}$$

where $F$ is the flow rate of the carrier gas in l/min, $S$ the chart speed in cm/min, $n$ the amount of sample injected in moles. $I_b$ and $I_e$ are the detector current without and with a capturing species in the detector, respectively. Since the detector signal proportional to $(I_b-I_e)$ was converted into the signal proportional to $(I_b-I_e)/I_e$ through an analog convertor,[3)] the integral term of the above equation corresponds to the peak area on the chromatogram.

## Results and Discussion

The mode of the electron capture reaction for a halogen compound depends upon the organic group bonding to the halogen atom. An aklyl halide captures a free electron dissociatively (Eq. 2), while an aryl halide dose so before the bond dissociation of the carbon-halogen bond (Eq. 3).[2,4)]

$$\mathrm{RX} + \mathrm{e}^- \longrightarrow \mathrm{R}\cdot + \mathrm{X}^- \tag{2}$$

$$\mathrm{ArX} + \mathrm{e}^- \longrightarrow \mathrm{ArX}^{\dot{-}} \longrightarrow \mathrm{Ar}\cdot + \mathrm{X}^- \tag{3}$$

The type of reaction can be judged by means of the Arrhenius plot of ln $K$. According to Wentworth's theory,[5)] the temperature dependence of $K$ is expressed by the following equations:

$$\ln K = \ln Z - E^*/RT \quad \text{(dissociative)}, \tag{4}$$

$$\ln KT^{3/2} = \ln Z + EA/RT \quad \text{(nondissociative)}, \tag{5}$$

where $E^*$ and $EA$ are activation energy and molecular electron affinity, respectively; $R$ is the gas constant, $T$ the absolute temperature of the detector and $Z$ the pre-exponential factor. The Arrhenius plot of ln $K$ might be linear with a negative slope of $E^*/R$ for the dissociative case and with a positive slope of $EA/R$ for the nondissociative case.

In a previous paper,[1)] it was proposed that the dissociative electron capture reaction of an alkyl halide can be assumed to be similar to the $S_N2$ reaction in solution and the sp$^3$ orbital on the α-carbon atom changes to an sp$^2$ orbital with the approach of a free electron to an alkyl halide. The linear relationship observed between the activation energy and the change in internal energy was explained.

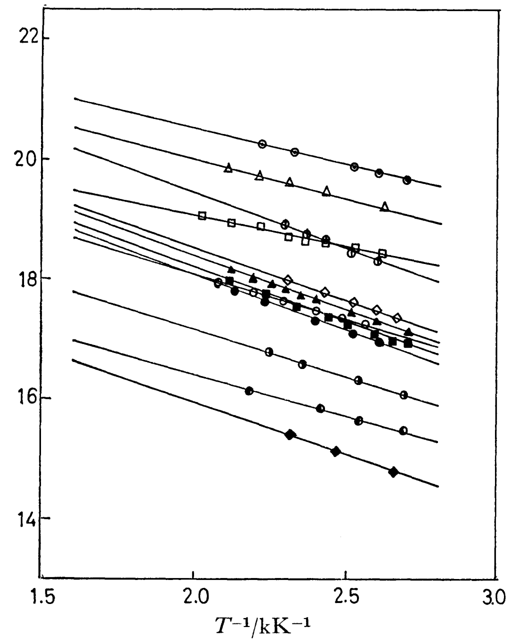


Fig. 1. Arrhenius plots of electron capture coefficients for benzyl chlorides.
● Benzyl chloride, ◆ *m*-methylbenzyl chloride, ○ *p*-methylbenzyl chloride, ▲ *p*-*t*-butylbenzyl chloride, △ *m*-chlorobenzyl chloride, ◑ *p*-chlorobenzyl chloride, ■ *m*-methoxybenzyl chloride, ◐ *p*-methoxybenzyl chloride, ⊙ *p*-phenylbenzyl chloride, △ *p*-cyanobenzyl chloride, ⦶ *m*-nitrobenzyl chloride, □ *p*-nitrobenzyl chloride.

It is of interest to see if this reaction model is adequate in the electron capture reaction of benzyl chlorides. It will be useful if the variation of activation energies for benzyl chlorides with various substituents is explained.

The Arrhenius plots of ln $K$ for benzyl chlorides with various substituents in the aromatic ring are shown in Fig. 1. Since all the plots are linear with negative slopes, benzyl chlorides capture free electron dissociatively as in the case of alkyl halides. The activation energies $E^*$ calculated by the least-squares method are given in Table 1.

Table 1. Activation energies for benzyl chlorides

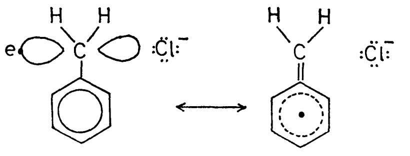
| Compound | $E^{*a)}$ / kcal mol$^{-1}$ |
|---|---|
| Benzyl chloride | $3.6 \pm 0.1^{b)}$ |
| *m*-Methylbenzyl chloride | $3.4 \pm 0.2$ |
| *p*-Methylbenzyl chloride | $3.2 \pm 0.2$ |
| *p*-Ethylbenzyl chloride | $3.1 \pm 0.2$ |
| *p*-Isopropylbenzyl chloride | $3.2 \pm 0.2$ |
| *p*-*t*-Butylbenzyl chloride | $3.6 \pm 0.1$ |
| *m*-Chlorobenzyl chloride | $3.5 \pm 0.2$ |
| *p*-Chlorobenzyl chloride | $3.0 \pm 0.1$ |
| *m*-Methoxybenzyl chloride | $3.6 \pm 0.1$ |
| *p*-Methoxybenzyl chloride | $3.0 \pm 0.1$ |
| *p*-Phenylbenzyl chloride | $2.5 \pm 0.2$ |
| *p*-Cyanobenzyl chloride | $2.6 \pm 0.1$ |
| *m*-Nitrobenzyl chloride | $3.5 \pm 0.2$ |
| *p*-Nitrobenzyl chloride | $2.0 \pm 0.1$ |

a) Activation energy. b) Standard deviation.

A question may be raised whether the α-carbon atom is the reaction center, or the α-carbon atom is attacked by a free electron. The activation energy of 8.6 kcal/mol[2)] or 9.25 kcal/mol[7)] observed for chlorobenzene corresponds to the energy of the barrier for electron attachment to the benzene nucleus of the compound. When the benzene nucleus is substituted by a more electron-withdrawing group, the electron attachment to the benzene nucleus occurs more easily.[2)] Therefore, when a free electron attacks the benzene nucleus of benzyl chloride, the activation energy should be greater than 8.6 kcal/mol. However, the activation energy of benzyl chloride is only 3.6 kcal/mol (Table 1). It can be concluded that in analogy with alkyl halides, the α-carbon atom is attacked by a free electron in the electron capture reaction of benzyl chloride.

All the activation energies of benzyl chlorides in Table 1 are smaller than those of alkyl chlorides by 6—8 kcal/mol. A comparison of $K$ shows that benzyl chloride reacts with a free electron faster than alkyl chlorides by a factor of 1000—3000. The enhanced reactivity of benzyl chloride over the corresponding alkyl chloride has also been observed in $S_N2$ reaction in solution.[8)]

It seems that the transition state of the dissociative electron capture reaction for benzyl chloride has a structure as shown in Scheme A. It is expected from the structure that the accepted odd electron on the α-carbon atom is delocalized by the overlapping of the π orbital on the benzene ring with the p orbital on the α-carbon atom and the stabilization of the transition state due to such resonance affords the enhanced reactivity for benzyl chloride.



Scheme A.

In the substituted benzyl chlorides, it is necessary to take into account the contribution of substituents to the resonance through the benzene ring. The substituent effect in the electron capture reaction can be illustrated

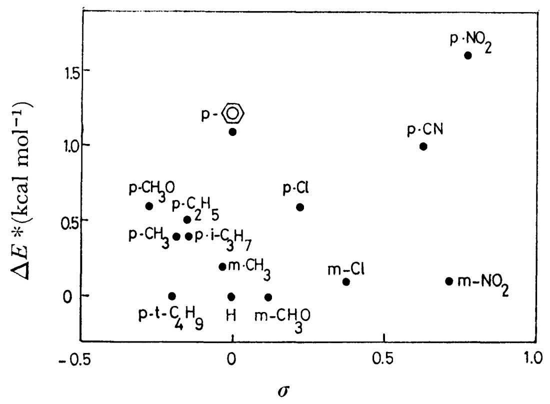


Fig. 2. Relationship between activation energy and Hammett substituent constant.

by a plot, $\Delta E^*$ $(=E_{\mathrm{H}}^*-E_{\mathrm{X}}^*)$ *vs.* the Hammett $\sigma$ constant, where the subscripts H and X are used to represent benzyl chloride and the benzyl chloride substituted by a group X, respectively (Fig. 2). The relationship between the electron capture coefficient $K$ and the rate constant $k$ in the dissociative electron capture reaction is given by

$$\ln K = \ln k_{12} - \ln k_{\mathrm{D}}, \tag{6}$$

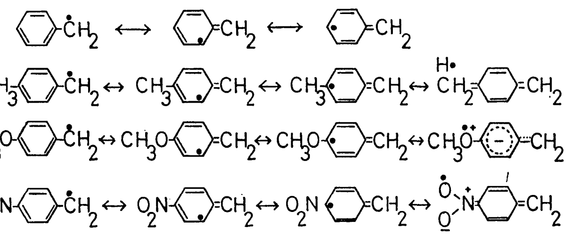
where $k_{\mathrm{D}}$ is the rate constant of the reaction between a positive ion produced from a molecule of the carrier gas and a free electron, $k_{12}$ is the rate constant of the dissociative process of benzyl chlorides as given by Eq. 2.[5–7] Using the Arrhenius equation, we have

$$\ln k_{12} = \ln Z' - \frac{E^*}{RT}. \tag{7}$$

$k_{\mathrm{D}}$ is almost temperature independent as pointed out by Wentworth and Chen.[5] Hence, $\ln(K_{\mathrm{X}}/K_{\mathrm{H}})$ is nearly equal to $\ln(k_{12,\mathrm{X}}/k_{12,\mathrm{H}})$. Since it is reasonable to presume that the pre-exponential factor $Z'$ is nearly equal for all the benzyl chlorides investigated, $\Delta E^*$ (ordinate, Fig. 2) is approximately equal to the difference in $\ln k_{12}$ between the benzyl chloride substituted by a group X and benzyl chloride. Thus, Fig. 2 can be considered to be Hammett plot which enables us to evaluate the substituent effect in the electron capture reaction.

We see that the plots for meta-substituted benzyl chlorides are linear with a slope near to zero. This can be explained as follows. In the transition state for benzyl chlorides, the negative charge is localized on the chlorine atom as shown in Scheme A. Consequently, a group in meta position does not contribute to the stabilization of the transition state by the inductive effect. The odd electron can conjugate only with the $\pi$ electrons in the aromatic ring and the conjugative system can not be extended to meta substituents. The resonance effect, therefore, for all meta-substituted benzyl chlorides should be equal to that for benzyl chloride itself.

On the other hand, no simple relation exists between $\Delta E^*$ and the Hammett $\sigma$ constant for para-substituted benzyl chlorides. The plot is concave downward. Both electron releasing groups except for *t*-butyl group and electron withdrawing groups tend to decrease the activation energy. This indicate that, in the transition state of para-substituted benzyl chlorides, the odd electron accepted on the $\alpha$-carbon atom can conjugate not only with the $\pi$ electrons in the aromatic ring, but with the electrons in the para substituent through the $\pi$ electron system of the aromatic ring. Consequently, para substituents contribute to the stabilization of the transition state through hydrogen atom hyperconjugation and electron donating or electron accepting resonance as shown in Scheme B. The resonance effect of the para substituents decreases in the order: $NO_2$>CN, $C_6H_5$ >$CH_3O$, Cl>*iso*-$C_3H_7$, $C_2H_5$, $CH_3$>H. As *t*-butyl group has no hydrogen atom capable of participating in the hyperconjugation, the resonance effect for *t*-butylbenzyl chloride is equal to that for benzyl chloride itself. The order is in line with that of the substituent effect found in polarographic reduction of benzyl halides.[9,10]



Scheme B.

A similar substituent effect has been reported in the phenylation of substituted benzenes with phenyl radical. Ito and coworkers observed that for all benzene compounds the ortho and para positions are more reactive than the meta position. The relative reactivity of the para position does not satisfy the Hammett relation, being usually larger than that expected from the Hammett equation by an increment of $\tau_{\mathrm{p}}$ as expressed by

$$\log\,(k_{\mathrm{X(p)}}/k_{\mathrm{H}}) = \rho\sigma_{\mathrm{p}} + \tau_{\mathrm{p}}, \tag{8}$$

where $k_{\mathrm{X(p)}}/k_{\mathrm{H}}$ is the partial rate constant of the para position of the benzene substituted by a group X in phenylation, $\rho$ is the Hammett reaction constant for the phenylation estimated from the Hammett plot for the meta substituent and $\sigma_{\mathrm{p}}$ is the Hammett substituent constant for para position.[11] $\tau_{\mathrm{p}}$ is regarded as a measure of the conjugative effect.

The value of $\tau_{\mathrm{p}}$ for a substituent is approximately constant for each substituted benzene irrespective of the nature of attacking radical. It is accepted that the homolytic phenylation proceeds through the rate determining step of the addition of a phenyl radical to the aromatic ring, a phenylcyclohexadienyl radical being formed as an intermediate. When the substitution occurs in the para position to a substituent, the odd electron in the transition state can conjugate with the electrons in the substituent. Consequently, the value of $\tau_{\mathrm{p}}$ indicates the extent to which the incipient radical in the transition state of the addition of a phenyl radical to a substituted benzene is stabilized by resonance.

Thus, $\Delta E^*$ and $\tau_{\mathrm{p}}$ can be considered to show identical character, and the validity of our proposal on the mechanism of the dissociative electron capture reaction for benzyl chlorides should be judged by a comparison of $\Delta E^*$ and $\tau_{\mathrm{p}}$. As shown in Table 2, the conjugative effect expressed in energy term $2.3RT\tau_{\mathrm{p}}$ is almost equal

TABLE 2. COMPARISON OF THE CONJUGATIVE EFFECT OF PARA-SUBSTITUENTS OBSERVED IN ELECTRON CAPTURE REACTION OF BENZYL CHLORIDES WITH THAT OBSERVED IN PHENYLATION OF SUBSTITUTED BENZENES BY PHENYL RADICAL

| Substituent | $\Delta E^{*a)}$ kcal mol$^{-1}$ | $\tau_p{}^{b)}$ | $2.3RT\tau_p{}^{c)}$ kcal mol$^{-1}$ |
|---|---|---|---|
| $CH_3$ | 0.4 | 0.09 | 0.2 |
| Cl | 0.5 | 0.16 | 0.3 |
| $CH_3O$ | 0.6 | 0.14 | 0.3 |
| $NO_2$ | 1.6 | 0.9 | 1.8 |

a) The conjugative effect of para substituents observed in electron capture reaction of benzyl chlorides. b) Values taken from Ref. 11. c) $T$=423 K.

to $\Delta E^*$ at 423 K, the average temperature of ECD. The agreement between $\Delta E^*$ and $\tau_p$ shows that our proposal is valid. Thus, the substituent effect is explained by assuming the reaction mechanism of the electron capture reaction for benzyl chlorides analogous to that of alkyl halides.

## Conclusion

An extensive study has been made on the substituent effect on the electron capture reaction of benzyl chlorides. We concluded that the electron capture reaction of benzyl chlorides is a kind of $S_N2$ reaction in analogy with alkyl halides. The enhanced reactivity of a para-substituted benzyl chloride over the corresponding meta isomer and benzyl chloride itself can be explained on the basis of a mechanism similar to the $S_N2$ reaction. Our proposal on the mechanism of the electron capture reaction will be useful for understanding the relationship between the activation energy measured and the chemical structure of the sample molecule and for identifying peaks on the chromatogram for separation of halogen compounds by GC-ECD system.

## References

1) T. Kojima, Y. Tanaka, and M. Satouchi, *Anal. Chem.*, **48**, 1760 (1976).
2) M. Satouchi and T. Kojima, *Bunseki Kagaku*, **25**, 764 (1976).
3) T. Kojima and M. Satouchi, *Bunseki Kagaku*, **22**, 1428 (1972).
4) W. E. Wentworth, E. Chen, and J. E. Lovelock, *J. Phys. Chem.*, **70**, 445 (1966).
5) W. E. Wentworth and E. Chen, *J. Gas. Chromatogr.*, **5**, 170 (1967).
6) W. E. Wentworth, R. S. Becker, and R. Tung, *J. Phys. Chem.*, **71**, 1652 (1967).
7) J. C. Steelhammer and W. E. Wentworth, *J. Chem. Phys.*, **51**, 1802 (1969).
8) R. G. Pearson, S. H. Langer, F. V. Williams, and W. J. McGuire, *J. Am. Chem. Soc.*, **74**, 5130 (1952).
9) G. Klopman, *Helv. Chim. Acta*, **44**, 1908 (1961).
10) A. Streitwieser, Jr. and C. Perrin, *J. Am. Chem. Soc.*, **86**, 4938 (1964).
11) R. Ito, T. Migita, N. Morioka, and O. Shimamura, *Tetrahedron*, **21**, 955 (1965).