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Significance of Steric Effect in the Heterolysis of Carbon–Carbon σ Bond in Ionically Dissociative Hydrocarbons

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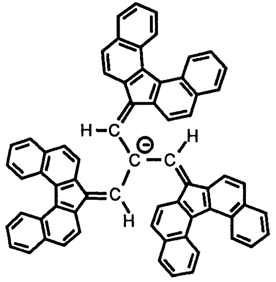
The standard free energies of heterolysis ($\Delta G°_{het}$) of a carbon-carbon σ bond in sterically congested hydrocarbons $\mathbf{R_1}$–$\mathbf{R_{2b-j}}$ and a related derivative $\mathbf{R_1}$–$\mathbf{R_{2a}}$ in DMSO and sulfolane at 25 °C are about 40 kJ / mol smaller than expected from Arnett's master equations, indicating the importance of steric factor in the heterolytic cleavage.

Heterolysis of a carbon-carbon σ bond to form a carbocation and a carbanion is of interest from thermodynamic1) and mechanistic2) points of view. Meanwhile, Arnett and his coworkers proposed an empirical relationship (master equation)3) to correlate heterolysis enthalpies with pK_{R^+}'s of cations and pK_a(RH)'s of anions.

Previously, we found that the hydrocarbon $\mathbf{R_1}$–$\mathbf{R_{2c}}$ (Fig. 1) heterolyzes into a stable carbanion $\mathbf{R_1}^-$ 4) and tropylium ion in DMSO.5) In the present study, we report the preparation and heterolysis of eight new ionically dissociative hydrocarbons $\mathbf{R_1}$–$\mathbf{R_{2b,d-j}}$ and a related bromo derivative $\mathbf{R_1}$–$\mathbf{R_{2a}}$ in DMSO and sulfolane. Determinations of the standard free energies of heterolysis ($\Delta G°_{het}$) for the C–C σ bond have shown that the steric effect plays a significant role in facilitating the heterolysis as well as the thermodynamic stabilities of cations and anions.



$\mathbf{R_1}^-$ (pK_a(RH) 5.9$^{4)}$)

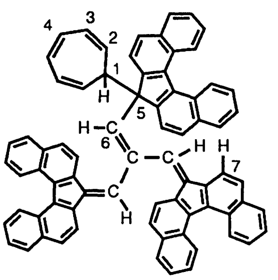
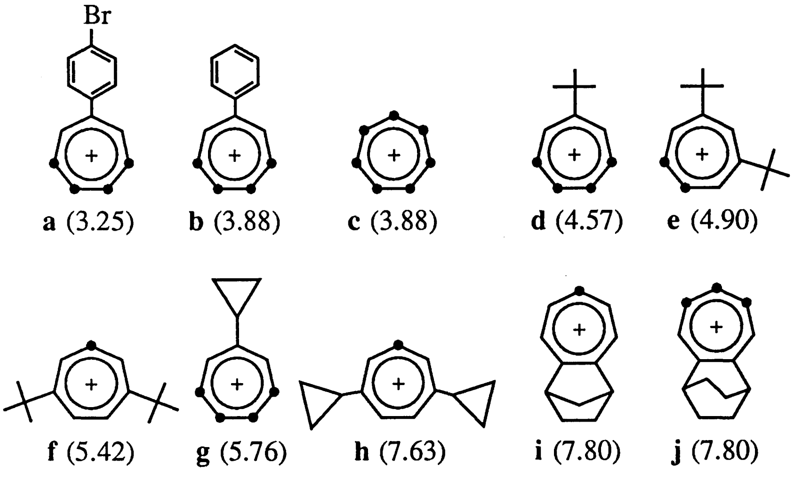


Fig. 1. Structure of covalent hydrocarbon $\mathbf{R_1}$–$\mathbf{R_{2c}}$.



$\mathbf{R_2}^+$ (pK_{R^+} in 50% aq. MeCN)$^{6,7)}$

The position indicated by a dot denotes the carbon forming the C–C σ bond.

Compounds $\mathbf{R_1}$–$\mathbf{R_{2a-j}}$ were prepared by mixing a deep green solution of $\mathbf{R_1}^-\mathrm{K}^+$, generated from $\mathbf{R_1}$H by treatment with *t*-BuOK in THF, and an equimolar amount of $\mathbf{R_2}^+\mathrm{ClO_4}^-$ (or $\mathrm{BF_4}^-$) in THF-MeCN under argon in the dark. Evaporation of the solvent and subsequent extraction with chloroform or benzene afforded $\mathbf{R_1}$–$\mathbf{R_{2a-j}}$ as reddish-orange solids in almost quantitative yields. Compounds $\mathbf{R_1}$–$\mathbf{R_{2a-f}}$ were purified further by TLC (SiO_2, benzene-hexane (1:1)) and reprecipitation (CH_2Cl_2-pentane) to give orange powders.[8)]

The structure assignment of the covalent products is based on ^{1}H NMR in $CDCl_3$.[9)] Compounds $\mathbf{R_1}$–$\mathbf{R_{2a-j}}$ showed a finely split triplet ($J \approx 1.4$ Hz) or a broad singlet at ≈6.6 ppm corresponding to the H–6 proton (see Fig. 1). Signals in the olefinic region indicated that the combination of $\mathbf{R_1}^-$ with $\mathbf{R_{2a}}^+$, $\mathbf{R_{2b}}^+$, $\mathbf{R_{2d}}^+$, $\mathbf{R_{2g}}^+$, or $\mathbf{R_{2j}}^+$ gave two isomers, in which $\mathbf{R_1}^-$ is connected to different positions in the seven-membered ring of the cation.[10)] Among aromatic proton signals a doublet (1 H, J = 7.8 – 9.3 Hz) observed at 6.5 – 6.6 ppm is notable. This signal can be assigned most probably to the highly shielded H–7 proton.

Table 1. The Concentration Equilibrium Constants (K_{het}) and Standard Free Energies of Heterolysis ($\Delta G°_{het}$) for Ionically Dissociative Covalent Compounds $\mathbf{R_1}$–$\mathbf{R_{2a-j}}$ in DMSO and Sulfolane at 25 °C

Compound	$10^6 K_{het}$ $(=[\mathbf{R_1}^-][\mathbf{R_2}^+]/[\mathbf{R_1}-\mathbf{R_2}])$/M DMSO	$10^6 K_{het}$ Sulfolane[b)]	$\Delta G°_{het}$ $(=-RT \ln K°_{het})$[c)]/kJ mol^{-1} DMSO	$\Delta G°_{het}$ Sulfolane[b)]	Predicted ΔH_{het}[d)] kJ mol^{-1}
$\mathbf{R_1}$–$\mathbf{R_{2a}}$[a)]	0.458 ± 0.017	—	36.2 ± 0.1	—	83.0
$\mathbf{R_1}$–$\mathbf{R_{2b}}$[a)]	1.09 ± 0.43	—	34.3 ± 1.0	—	82.2
$\mathbf{R_1}$–$\mathbf{R_{2c}}$	0.863 ± 0.078	—	34.7 ± 0.2	—	82.2
$\mathbf{R_1}$–$\mathbf{R_{2d}}$[a)]	1.06 ± 0.24	0.174 ± 0.039	34.2 ± 0.6	38.7 ± 0.6	81.2
$\mathbf{R_1}$–$\mathbf{R_{2e}}$	1.04 ± 0.04	0.199 ± 0.059	34.2 ± 0.1	38.4 ± 0.8	80.8
$\mathbf{R_1}$–$\mathbf{R_{2f}}$	2.20 ± 0.42	1.41 ± 0.27	32.4 ± 0.5	33.5 ± 0.5	80.1
$\mathbf{R_1}$–$\mathbf{R_{2g}}$[a)]	6.66 ± 0.90	1.40 ± 0.08	29.6 ± 0.3	33.5 ± 0.1	79.6
$\mathbf{R_1}$–$\mathbf{R_{2h}}$	258 ± 6	13.8 ± 3.8	20.6 ± 0.1	28.0 ± 0.7	77.1
$\mathbf{R_1}$–$\mathbf{R_{2i}}$	159 ± 55	22.2 ± 11.3	22.0 ± 0.9	27.0 ± 1.4	76.8
$\mathbf{R_1}$–$\mathbf{R_{2j}}$[a)]	124 ± 20	26.0 ± 17.3	22.4 ± 0.4	27.0 ± 2.0	76.8

a) Mixture of two isomers. b) Contains 5% (v/v) of 3-methylsulfolane. c) $K°_{het} = K_{het} \times (\gamma\pm)^2$. d) Predicted by using the master equation in Ref. 3.

When $\mathbf{R_1}$–$\mathbf{R_{2a-j}}$ was dissolved (10^{-5} – 10^{-4} M) in polar solvents such as DMSO or sulfolane,[11)] the deep green color of $\mathbf{R_1}^-$ (λ_{max} (DMSO or sulfolane) 697 nm, log ε 5.18) developed. The thermodynamic equilibrium constants ($K°_{het}$) were calculated by using equation $K°_{het} = K_{het} \times (\gamma\pm)^2$, where K_{het} is the concentration equilibrium constant ($[\mathbf{R_1}^-][\mathbf{R_2}^+]/[\mathbf{R_1}-\mathbf{R_2}]$) and $\gamma\pm$ the mean activity coefficient obtained by the Debye-Hückel limiting law equation. The thermodynamic equilibrium constant is essentially constant for different concentrations ranging from 10^{-5} to 10^{-4} M, indicating reversible heterolysis to produce $\mathbf{R_1}^-$ and $\mathbf{R_2}^+$. In sulfolane, a small amount of radical $\mathbf{R_1}\cdot$ (0.5 – 11%, λ_{max} (DMSO) 551 nm, log ε 5.04) formed presumably owing to impurities in sulfolane; its concentration was added to that of $\mathbf{R_1}^-$ for the calculation of K_{het}. Although the concentration of

$\mathbf{R_1}^-$ showed a small temperature dependence in DMSO, gradual decomposition of $\mathbf{R_2}^+$ did not allow accurate determination of $\Delta H°_{het}$ and $\Delta S°_{het}$. Table 1 summarizes the K_{het} and $\Delta G°_{het}$ ($=-RT \ln K°_{het}$) for $\mathbf{R_1}$–$\mathbf{R_{2a-j}}$ at 25 °C.[12)]

Recently, Arnett and his coworkers determined the heats of reactions of various carbocations with carbanions in MeCN or sulfolane, and found that the enthalpy of heterolysis of a C–C σ bond can be expressed by "master equations" consisting of linear combination of pK_{R^+}'s of carbocations and pK_a(RH)'s of carbanions.[3)] It was uncertain, however, if these equations could be applied to the present system, since they were derived by using sterically unencumbered ions.

For secondary cations: ΔH_{het} (kcal / mol) = $13.18 - 0.324(pK_{R^+}) + 1.307(pK_a)$ (1)

For tertiary cations : ΔH_{het} (kcal / mol) = $8.895 - 0.648(pK_{R^+}) + 1.294(pK_a)$ (2)

Figure 2 shows the plot of $\Delta G°_{het}$ values of Table 1, together with the lines expressed by Eqs. 1 and 2 for ΔH_{het}. The tropylium ions are categorized to secondary cations; therefore, our $\Delta G°_{het}$ values should be assessed by using Eq. 1. Direct comparisons of $\Delta G°_{het}$ values and ΔH_{het} ones seem to be reasonable since $\Delta S°_{het}$ values have been found to be very small and $\Delta G°_{het}$ values approximate to ΔH_{het} ones within 4 kJ/mol in Arnett's system.[13),14)] As shown in Fig. 2, $\Delta G°_{het}$ values for $\mathbf{R_1}$–$\mathbf{R_{2a-j}}$ are smaller than those expected from Eq. 1 by approximately 40 kJ / mol (predicted ΔH_{het} values are shown in Table 1). This discrepancy is most probably ascribed to steric congestion in the hydrocarbons composed of $\mathbf{R_1}^-$ and $\mathbf{R_2}^+$.

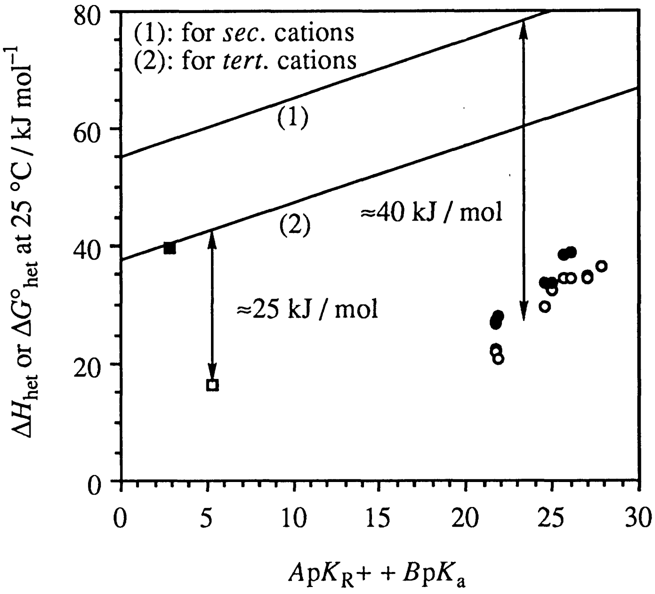


Fig. 2. Plot of $\Delta G°_{het}$ on the master equation scale: open circle, $\mathbf{R_1}$–$\mathbf{R_{2a-j}}$ in DMSO; closed circle, $\mathbf{R_1}$–$\mathbf{R_{2a-j}}$ in sulfolane; open square, tri-*t*-butylcyclopropenylium ion + phenylmalononitrile ion (in MeCN); closed square, trimethylcyclopropenylium ion + phenylmalononitrile ion (in MeCN). All energy terms are converted to kJ / mol.

A similar steric effect is naturally expected to arise from bulky substituents in the cationic moiety. This was indeed observed when tri-*t*-butylcyclopropenylium ion (pK_{R^+} 6.5[15)] in 50% aq. MeCN) and phenylmalononitrile anion (pK_a(RH) 4.24[13)]) were mixed in MeCN in a cell sealed under vacuum and $K°_{het}$ was determined;[16)] the $\Delta G°_{het}$ was 16.3 kJ / mol, which is smaller than the ΔH_{het} calculated from Eq. 2 by ≈25 kJ / mol (see Fig. 2).

In contrast, according to Arnett's data,[13)] the $\Delta G°_{het}$ to form less hindered trimethylcyclopropenylium ion and phenylmalononitrile ion in MeCN has been nicely accommodated to the line of Eq. 2 (see Fig. 2). Thus, besides the electronic stabilities of generated carbocations and carbanions, the steric congestion has been shown to play a significant role in facilitating C–C σ bond heterolysis of ionically dissociative covalent compounds. The importance of steric congestion in lowering the homolytic dissociation energy for a C–C σ bond has been pointed out by Rüchardt on the basis of systematic studies.[17]

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8) Purity of $\mathbf{R_1}$–$\mathbf{R_{2a-f}}$ was confirmed by satisfactory elemental analysis and ^{1}H NMR. On the other hand, $\mathbf{R_1}$–$\mathbf{R_{2g-j}}$ were not stable enough to be purified by TLC or reprecipitation. Their purity (contains <5 % THF by weight) was checked by ^{1}H NMR.
9) Previously reported ^{1}H NMR data for $\mathbf{R_1}$–$\mathbf{R_{2c}}$[5] were revised as follows (CDCl$_3$, 300 MHz): δ 8.84 – 7.02 (m, 37 H, aromatic and olefinic protons), 6.592 (d, 2 H, H–4, J = 3.0 Hz), 6.591 (d, 1 H, H–7, J = 8.4 Hz), 6.52 (t, 1 H, H–6, J = 1.4 Hz), 6.06 (dd, 2 H, H–3, J = 9.3, 3.0 Hz), 5.21 (dd, 2 H, H–2, J = 5.7, 9.3 Hz), 2.72 (t, 1 H, H–1, J = 5.7 Hz). ^{13}C NMR (CDCl$_3$, 25 MHz) δ 146.8 – 117.5 (aromatic and olefinic carbons), 58.2 (s, C–5), 47.8 (d, C–1).
10) Less hindered 4-substituted products were major. For $\mathbf{R_{2a}}^+$, $\mathbf{R_{2b}}^+$, $\mathbf{R_{2d}}^+$, $\mathbf{R_{2g}}^+$, and $\mathbf{R_{2j}}^+$, the fractions of the major products, determined by integration of H–1 signals, were 55, 60, 65, 70, and 50%, respectively. The single product from $\mathbf{R_{2i}}^+$ is due to the strained structure of cycloheptatriene moiety compared with that from $\mathbf{R_{2j}}^+$.
11) 3-Methylsulfolane (5% by volume) was added to prevent sulfolane from freezing.
12) The behavior as a weak electrolyte was also demonstrated for $\mathbf{R_1}$–$\mathbf{R_{2c}}$, $\mathbf{R_1}$–$\mathbf{R_{2e}}$, and $\mathbf{R_1}$–$\mathbf{R_{2f}}$ by electric conductivity measurement in DMSO (10^{-5} – 10^{-4}M) at 25 °C under argon.
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