

Review Commentary

Structural dependence of heterolytic bond dissociation energy of carbon–carbon σ bonds in hydrocarbons

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ABSTRACT: The coordination of a resonance-stabilized hydrocarbon cation and anion yielded a series of unprecedented hydrocarbons, which are susceptible to thermal heterolytic cleavage of carbon–carbon σ bonds in polar media, generating the original ions under reversible conditions. When the component ions were sufficiently stabilized, some ion pairs were even isolated as solids, thus providing the first examples of hydrocarbon salts. The direct observation of the heterolysis by means of spectroscopy permitted reliable thermodynamic treatments of the observed degree of ionic dissociation. Correlation of the free energy of heterolysis with solvent dielectric constants and parameters of ion stabilities such as pK_{HA} , pK_{R^-} and redox potentials revealed the importance of the thermodynamic stabilities of ions, the degree of solvation and steric congestion in the starting molecule as major controlling factors in the heterolysis. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: heterolytic bond dissociation energy; carbon–carbon σ bonds; hydrocarbons; structural dependence

INTRODUCTION

Hydrocarbons constitute the most fundamental group of compounds in organic chemistry. As expressed in the introductory portions of many textbooks, carbon–carbon bonds in such molecules are thought to be covalent in nature, and the standard mode of thermal cleavage of these bonds is homolysis (Scheme 1). Considering the electrically neutral character of carbon atoms, however, it would not be surprising to observe the heterolysis of a carbon–carbon bond in hydrocarbons for the case of a properly designed structure. Carbon is positioned in the middle of the first row of the Periodic Table, between a series of electropositive (Li, Be and B) and electronegative (N, O and F) elements. As a result, carbon is amphoteric in nature, which permits the formation of trivalent, carbon-centered Lewis acidic (carbenium ion) and Lewis basic (carbanion) species. In view of the noticeable tendency for carbon to form both types of species, the carbon–carbon bond may be considerably susceptible to thermal heterolysis, a phenomenon which is uncommon in a bond connecting atoms of the same

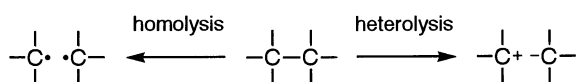
element. It might be expected for this reason that small electrical imbalances, caused by the influence of substituents and solvent, between the ends of carbon–carbon bonds may induce polarization, thus permitting the experimental observation of heterolytic cleavage to form a pair of ions.

Usually, carbocations and carbanions are highly reactive, but are stabilized by resonance so that one can detect them in solution as long-lived entities. To date, a number of extremely stable carbon ions have been reported.¹ It is natural to consider that the most straightforward method for obtaining a heterolytically dissociative hydrocarbon is to construct a molecule by connecting highly stable cationic and anionic hydrocarbon moieties. In this review, the synthesis of such hydrocarbons and the direct observation of their heterolysis in solution or in the solid state will be described. Factors that govern heterolytic bond dissociation energy will be discussed in a quantitative manner, based on the thermodynamic parameters determined under reversible conditions.

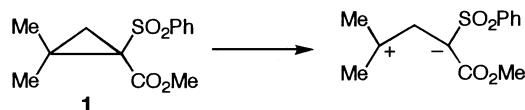
HISTORICAL CONTEXT

The first proposals for the heterolytic dissociation of a carbon–carbon bond date back to the 1960s, when the thermal ring opening of cyclopropane (**1**), cyclobutane (**2**), and norbornadiene (**3**) derivatives in polar solvents were independently reported by the groups of Cram,² Huisgen,³ and Hoffmann⁴ and Lemal,⁵ respectively

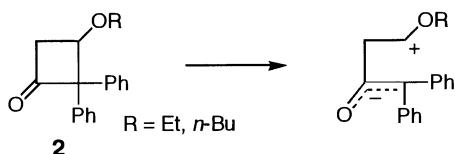
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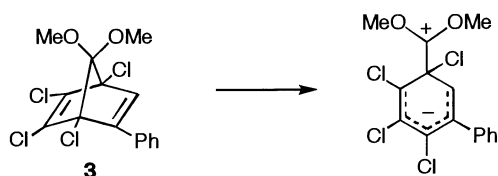
Scheme 1



1



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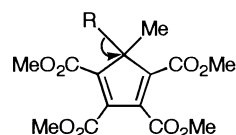


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Scheme 2

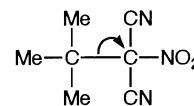
(Scheme 2). Compared with the vast number of examples of homolytic cleavage, only a limited number of examples of the heterolysis of carbon-carbon bonds can be found in the literature, even today, and most of these are related to the thermal cleavage of small-ring systems. Relief of strain by ring opening is obviously a fundamental driving force for this type of bond dissociation. The presence of a strongly electron-donating substituent on one side of the dissociating carbon-carbon bond and of a strongly electron-withdrawing substituent on the other makes heterolytic cleavage more favorable than homolytic cleavage, since the zwitterion intermediates are sufficiently stabilized by delocalization of positive and/or negative charges.

Alternatively, an ionic intermediate is stabilized by



R = Ph₂CH, MeOCH₂,
1-adamantyl, *p*-MeOC₆H₄CH₂

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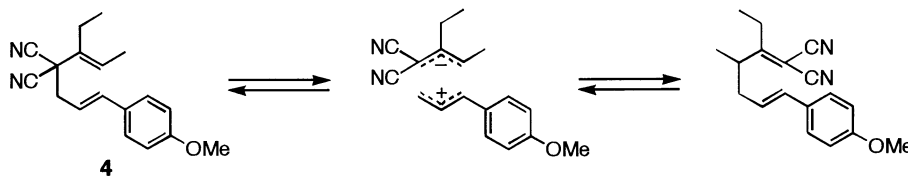
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delocalization of the positive or the negative charge to form a charged Hückel system such as cyclopropenylum, tropylium and cyclopentadienide ions, in addition to other π -conjugated systems, such as allyl and cyclohexadienyl.

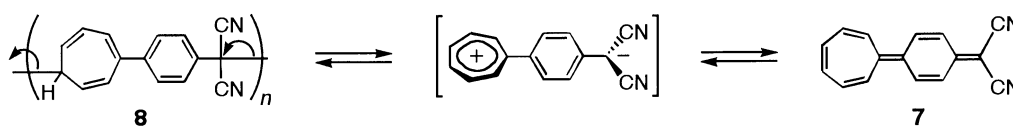
If sufficient stabilization of ions is achieved, heterolysis can also be observed in non-strained systems. This allows the occurrence of reactions that are thought to take place through a concerted pathway by an ionic fragmentation-recombination mechanism. Such a mechanism has been proposed for the Cope rearrangement of **4** (Scheme 3).⁶ Another example is the ionic 1,5-shift in **5**,⁷ where an alkyl cation migrates on to a cyclopentadienyl ring. In these examples, charges in the proposed ionic intermediates are efficiently spread over suitably located heteroatom substituents.

One of the simplest reactions initiated by heterolysis is the S_N1-type solvolysis, in which a carbanion acts as a leaving group. Some examples of such reactions have been reported by Mitsuhashi and Hirota⁸ for **6** and other compounds, which eject an anion stabilized by cyano and nitro groups.

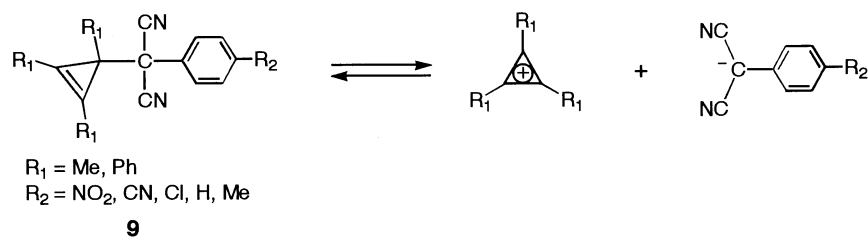
Takahashi and co-workers⁹ reported that the quinoid compound **7**, having a cycloheptatrienyldiene and a dicyanomethylene group, readily forms cyclic oligomers **8** in a concentrated or cooled solution. This oligomerization is reversible at lower concentrations or at high temperatures, regenerating monomer **7**. A twisted zwitterionic intermediate, in which the tropylium ion and the malononitrile anion are connected by a *p*-phenylene group, has been suggested (Scheme 4).



Scheme 3



Scheme 4



Scheme 5

In the reactions mentioned above, the formation of a transient ionic intermediate was proposed, but not directly observed. The ionic mechanism was distinguished from the formation of a radical intermediate by the examination of solvent and substituent effects and trapping experiments. On the other hand, the first example of *reversible* heterolysis of a carbon–carbon bond was reported by Arnett *et al.*¹⁰ in 1983. They found that **9** dissociates into a cyclopropenyl cation and an arylmalononitrile anion when dissolved in a polar solvent (Scheme 5). These workers also demonstrated that equilibrium between the covalent molecule and the ion pair can be observed, provided that the generating ions are reasonably stabilized.

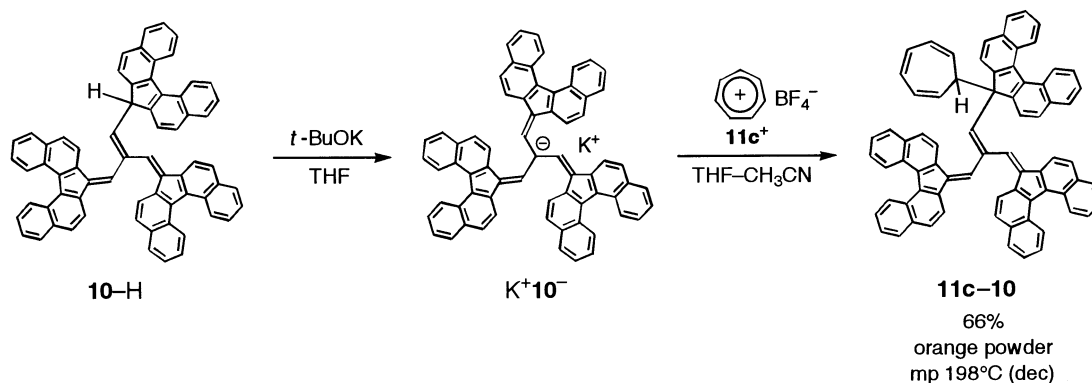
HYDROCARBONS THAT UNDERGO REVERSIBLE HETEROLYSIS OF CARBON–CARBON BONDS

The first synthesis of heterolytically dissociative hydrocarbon

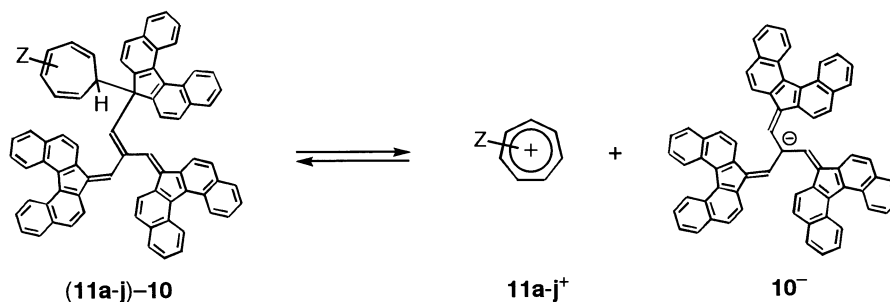
The observation of the ionic dissociation of **9** posed the possibility that hydrocarbons might also dissociate ionically into a stable carbocation and carbanion, provided that the ions are highly stable and the medium is sufficiently polar. The first observation of the ionic dissociation of the carbon–carbon σ bond in a hydrocarbon was reported in 1985 for the compound **11c–10**.¹¹

This hydrocarbon was synthesized by mixing individually prepared component ions, *i.e.* the tropylium ion **11c**⁺ and Kuhn's carbanion **10**[−].¹² Initially, a deep green solution of $\text{K}^+\text{10}^-$ was generated in THF from the parent hydrocarbon (**10–H**, orange powder) by deprotonation with *t*-BuOK. An equimolar amount of a carbocation salt (**11c**⁺ BF_4^-) in THF–acetonitrile (1:1) was then added to the solution. The deep green color of **10**[−] immediately vanished and the solution became orange, indicating the formation of a covalent product (Scheme 6). The inorganic component (KBF_4) was removed by evaporation of the solvent and subsequent extraction with chloroform. The product was successfully purified by TLC and subsequent reprecipitation (CH_2Cl_2 –pentane) to give an analytically pure hydrocarbon, **11c–10**, as an orange powder in 66% yield. The structure of the hydrocarbon was determined as indicated in Scheme 6 on the basis of ¹H and ¹³C NMR spectra.

A striking feature of this hydrocarbon is its ionization into **11c**⁺ and **10**[−] in polar media (Scheme 7, Z = H). The ionization was easily observed by the rapid development of a green color when the hydrocarbon was dissolved in polar solvents such as DMSO and sulfolane. The visible-region absorption spectra clearly exhibited the formation of **10**[−] ($\lambda_{\text{max}} = 697 \text{ nm}$, $\epsilon = 153\,000$) to an extent of 5% in DMSO. Acetone is not sufficiently polar to induce dissociation, but the solution became greenish colored when pyrene was added to the solution: a charge-transfer complex is formed between the tropylium ion and pyrene, shifting the equilibrium towards dissociation.



Scheme 6



Scheme 7

Other heterolytically dissociative hydrocarbons

The properties of the tropylium ion can be changed substantially by introducing various substituents on the seven-membered ring.¹³ The tropylium ion system is thus ideal for studying how the stability of the cationic moiety affects carbon–carbon bond heterolysis. Hydrocarbons **11b–10** and **(11d–j)–10** and a related bromo derivative **11a–10** were synthesized in a similar manner by mixing the anion **10⁻** with the substituted tropylium ions **11a⁺**, **11b⁺** and **11d⁺–j⁺**.^{14,15} Another stable hydrocarbon anion, **12⁻**,¹⁶ derived from fullerene (C₆₀), also gave ionically dissociative hydrocarbons with tropylium ions **11c⁺**, **11f⁺** and **11h⁺** (Scheme 8).^{17,18} Partial dissociation of these fullerene derivatives to generate **12⁻** ($\lambda_{\max} = 995 \text{ nm}$, $\epsilon = 2400$) was observed spectrophotometrically in 4:1 (v/v) DMSO–CS₂.

Similarly, cyclopropenylum ions, stabilized by cyclopropyl groups, give hydrocarbons, which, when dissolved in polar solvents, dissociate into ions. Thus far, four dissociative hydrocarbons and related compounds have been prepared from **13a–d⁺** and **10⁻** (Scheme 9).^{19,20} In

addition, coordination of **13e⁺** or **14⁺** with **12⁻** gave an ionically dissociative hydrocarbon containing a fullerene skeleton (Scheme 10).²¹

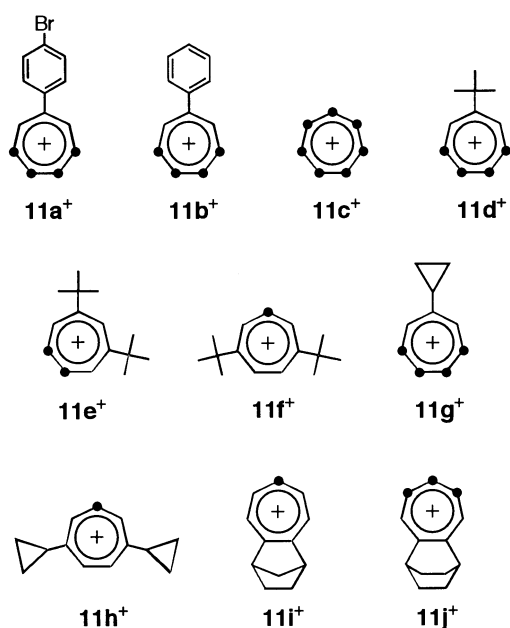
The structures of the coordination products shown in Schemes 6–10 were verified by NMR and IR spectra. In all the compounds derived from **10⁻** the cycloheptatrienyl or cyclopropenyl group is not attached at the central carbon of **10⁻**, but rather at an allylic position. Hydrocarbons obtained from **11a⁺**, **11b⁺**, **11d⁺**, **11g⁺** and **11j⁺** were mixtures of two positional isomers, in which **10⁻** is connected to different positions of the seven-membered ring. The positions indicated by dots on the structural formulas of these cations represent the carbons forming the carbon–carbon σ bond with **10⁻**.

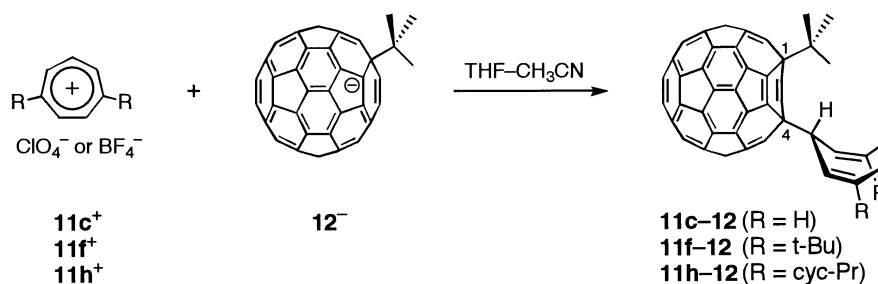
Cations **13a–d⁺** have, at first sight, two reaction sites, *i.e.* the cyclopropenylum ring carbon bearing the aryl group, C-1, and that bearing the cyclopropyl group, C-2. The coordination with **10⁻** and **12⁻**, however, took place exclusively on the latter carbon, owing to the steric hindrance by the aryl group, which prevents the cation from coordinating at C-1, and the relatively higher positive charge distribution on C-2, as indicated by the significant downfield shift of its ¹³C NMR signal. The addition of a carbocation on fulleride ion **12⁻** also occurred regioselectively, giving only the 1,4-adduct. It should be also mentioned that **13e–12** consists of two diastereomers because both the cationic and anionic moieties have a chiral center.

Reversible heterolysis of the carbon–carbon σ bond was observed for all these compounds. One can determine the degrees of dissociation from the characteristic absorptions of carbanion in the visible/near-IR region. In addition, electrical conductivity measurements for some of these hydrocarbons indicate that they behave as weak electrolytes (see below).

HYDROCARBON SALTS

Considering the ease of dissociation of the carbon–carbon σ bond of specially designed hydrocarbons into resonance-stabilized ions, we expected that extraordinarily stabilized ions can co-exist in solution in the absence of coordination. In such a case, it should be possible to





Scheme 8

isolate carbocation–carbanion salt, if the inorganic counterions and solvent could be successfully removed. Only limited examples of such organic salts are found in the literature.²² For these salts, the cationic and/or anionic moieties are stabilized by strongly electron-donating or electron-withdrawing substituents containing heteroatoms. No hydrocarbon was known to form an ionic solid.

To obtain the first example of such a hydrocarbon, *i.e.* a hydrocarbon salt, in 1985, we employed the combination of the most stable hydrocarbon cation and anion known at that time.¹¹ It had been reported that the tricycloppropylcyclopropenyl cation **14⁺** ($pK_{R^+} = 10.0$) gives a covalent compound with CN^- ($pK_{\text{HA}} = 9.14$) but not with the *p*-nitrophenoxide ion ($pK_{\text{HA}} = 7.2$).²³ Consequently, we expected that a hydrocarbon salt could be isolated by combining the stabilized hydrocarbon ions if the difference between the pK_{R^+} of the cation and the pK_{HA} of the anion is ≥ 3 .

Kuhn's hydrocarbon anion **10⁻**, which had been the most stable known hydrocarbon anion and has a pK_{HA} of 5.9,¹² was obviously a strong candidate for the anionic moiety. Actually, the first synthesis of a hydrocarbon salt

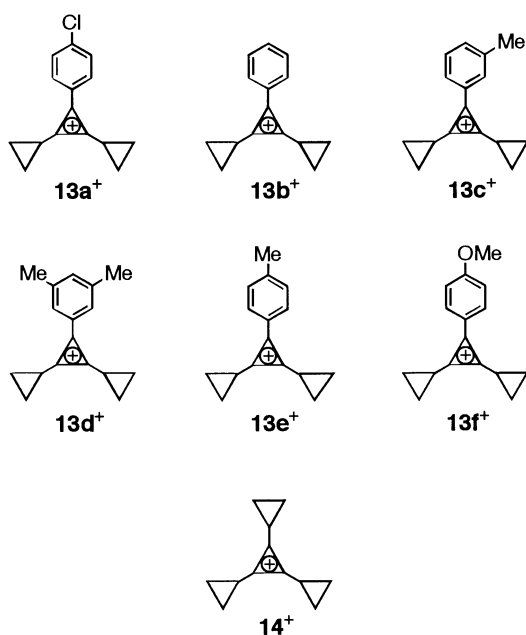
was achieved by combining this anion with tris(3-guaiazulenyl)cyclopropenyl cation **15⁺**. It was expected that, for cation **15⁺**, first synthesized by Agranat and Aharon-Shalom,²⁴ the three guaiazulenyl groups would effectively raise the thermodynamic stability of the cation and also increase steric congestion around the positive charge. Its pK_{R^+} value of 13.6²⁵ ranks it as one of the most stable hydrocarbon cations known today. To obtain the salt **15⁺10⁻**, a THF solution of K^+10^- and that of **15⁺** ClO_4^- were mixed under argon in the dark, instantly giving a mixture of KClO_4 and **15⁺10⁻** as a black precipitate. The salt **15⁺10⁻** was isolated by recrystallization from DMSO as greenish black needles in a yield of 61%.^{11,26}

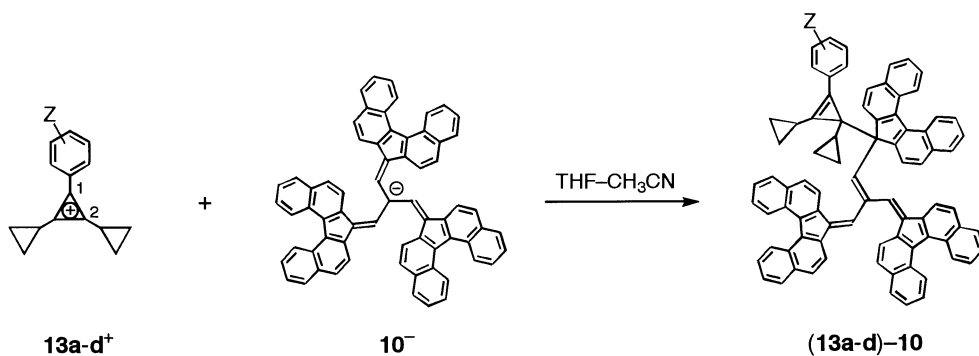
In a similar manner, four other hydrocarbon salts containing **10⁻** as the anionic component have been prepared in analytically pure forms (or as a monohydrate in the case of **18⁺**) from a series of cyclopropenyl cations, **13e⁺** ($pK_{R^+} = 7.29$),^{19,20} **14⁺** (10.0)^{26,27} and **16⁺** (8.9)²⁶ and tropylium ions **17⁺** (8.72)^{26,28} and **18⁺** (13.0).²⁹ A related carbocation–carbanion salt has been obtained from **13f⁺** and **10⁻**.²⁰ Similarly, fulleride ion **12⁻** ($pK_{\text{HA}} = 5.7$) gave a hydrocarbon salt by combining it with **15⁺**.^{21,30}

The salt structures of the solids obtained were confirmed by IR spectroscopy. The infrared absorption spectra of the solids, measured using KBr disks, were superimposable with the sum of the spectra of the corresponding cationic and anionic components, indicating that the solids are ionic materials R_1^+R_2^- rather than covalent compounds $\text{R}_1\text{-R}_2$.

The visible/near-IR absorption spectra for transparent KBr disks of salts **13e⁺10⁻**, **13f⁺10⁻** and **15⁺12⁻** showed absorptions corresponding to the cation (**15⁺**, $\lambda_{\text{max}} = 485$ nm; however, **13e⁺** and **13f⁺** have no absorption maxima in the visible/near-IR region) and the anion (λ_{max} : **10⁻**, 697 nm; **12⁻**, 1020 nm). No charge-transfer band was observed in the longer wavelength region, indicating that the solids can be classified as charge-separated salts, rather than charge-transfer complexes.

The electronic spectra measured for DMSO solutions ranging from the UV to the near-IR region agree with those of the component cation and anion superimposed, except that **13e⁺10⁻** and **13f⁺10⁻** underwent partial





Scheme 9

coordination in DMSO into the covalent forms **13e-10** and **13f-10**, respectively, whose structures are similar to **(13a-d)-10** (see Scheme 9), as indicated by the presence of only *ca* 90% of the theoretical amount of **10⁻** at a concentration of *ca* 10^{-4} M.

ELECTRICAL CONDUCTIVITY

Another piece of evidence indicating partial dissociation of **11c-10**, **11e-10** and **11f-10** in DMSO was provided by electrical conductivity measurements.¹⁵ The plot of molar conductivity (Λ) against square root of concentration, c (Onsager plot) gave curved lines, which are characteristic of weak electrolytes (Fig. 1). This result is in contrast to the linear relationship generally observed for strong electrolytes, such as the perchlorate salts of **11c⁺**, **11e⁺** and **11f⁺**. Extrapolation of Λ , obtained for the perchlorate salts, to $c=0$ in the $\Lambda-c^{1/2}$ plot gives the limiting molar conductivity Λ_0 (Table 1). Subtracting the molar conductivity for ClO_4^- in DMSO, $24.52 \text{ S cm}^2 \text{ mol}^{-1}$, from the observed Λ_0 for these salts yields the Λ_0

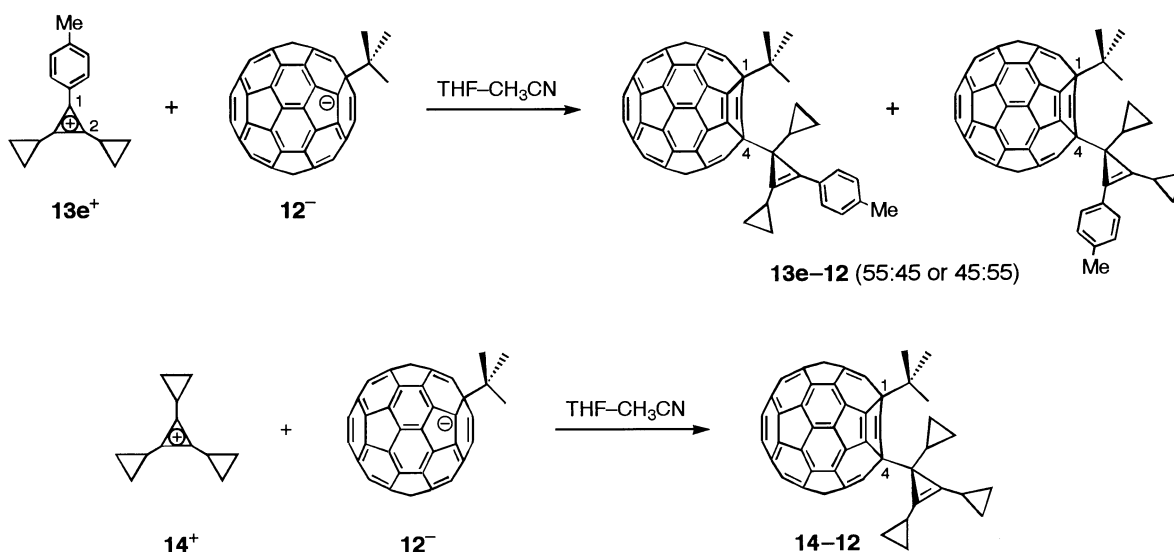
for the carbocations. Conductance measurements for hydrocarbon acid **10-H** indicated that this hydrocarbon is also a strong electrolyte in DMSO, giving a Λ_0 of $19.9 \text{ S cm}^2 \text{ mol}^{-1}$. This implies that hydrocarbon **10-H** actually behaves as a pair of free ions, H^+ and **10⁻**, in DMSO. Subtracting $14.6 \text{ S cm}^2 \text{ mol}^{-1}$, the Λ_0 of H^+ , affords the Λ_0 of **10⁻**, $5.3 \text{ S cm}^2 \text{ mol}^{-1}$.

The Λ_0 values for the cation and anion enabled us to determine the degrees of dissociation:

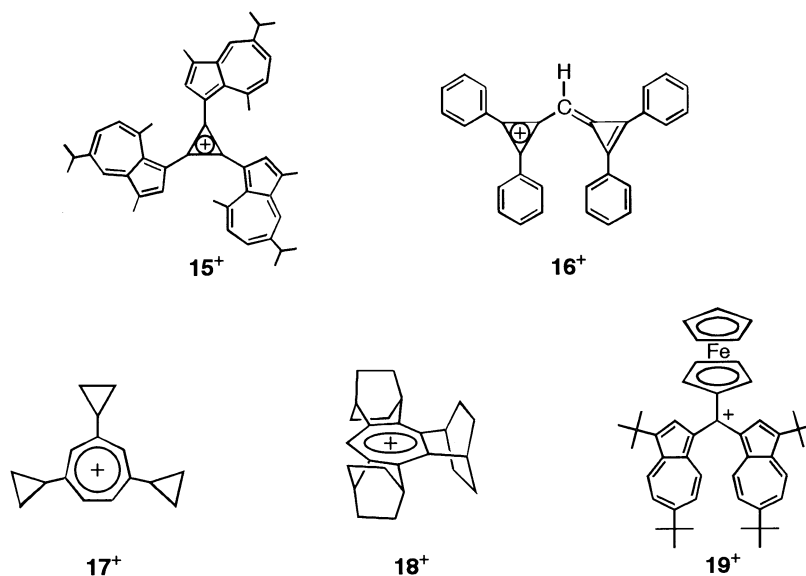
$$\alpha = \Lambda_c / [\Lambda_0(\text{cation}) + \Lambda_0(\text{anion})]$$

where Λ_c is the observed conductance at total concentration c . Equilibrium constants for heterolysis, K_{het} , obtained by equation $K_{\text{het}} = c\alpha^2/(1-\alpha)$, for **11c-10**, **11e-10** and **11f-10** are 0.6×10^{-6} , 2.3×10^{-6} and 5.9×10^{-6} M, respectively. These values are roughly in agreement with the spectrophotometrically obtained equilibrium constants (0.86×10^{-6} , 1.0×10^{-6} and 2.2×10^{-6} M, respectively; see below).

In contrast to above-mentioned hydrocarbons, hydrocarbon salts **14⁺10⁻** and **15⁺10⁻** followed Onsager's equation, indicating that they are *strong* electrolytes in



Scheme 10



DMSO, giving Λ_0^\pm values of 18.2 and 10.9 at 25.0°C, respectively. The Λ_0 values for 14^+ and 15^+ were determined to be 12.0 and 5.7 S cm² mol⁻¹ in a manner similar to that described above, using their perchlorate salts. These data, together with the Λ_0 of 10^- , 5.3 S cm² mol⁻¹, afford predicted values of 17.3 and 11.0 S cm² mol⁻¹. The good agreement of the observed limiting molar conductivities with the predicted values (Table 1) indicates that hydrocarbon salts 14^+10^- and 15^+10^- are over 99% dissociated in DMSO at concentrations of 10^{-4} – 10^{-5} M.²⁶

Earlier spectrophotometric data for complete dissociation of 14^+10^- were inconclusive, because the cation 14^+ shows no absorption in the region above 220 nm^{23,31} and, as a result, this method cannot be used to unequivocally demonstrate its presence. The above conductivity,

however, provides convincing evidence for the presence of both 14^+ and 10^- as dissociated ions.

Recently, Ito *et al.*³² have prepared a charge-transfer salt composed of 19^+ and 10^- and obtained a powder conductivity of 2.6×10^{-5} S cm⁻¹. Conductivity measurements using compressed powders of $13e^+10^-$ and 15^+12^- showed that these salts are also conductors, but the observed conductivities were smaller by at least one order of magnitude.^{25,33}

FACTORS THAT GOVERN THE FREE ENERGY OF HETEROLYSIS

Free energy, enthalpy and entropy of heterolysis

The success in observing reversible ionic dissociation of hydrocarbons having well defined structure enabled us to determine the thermodynamic properties for the carbon–

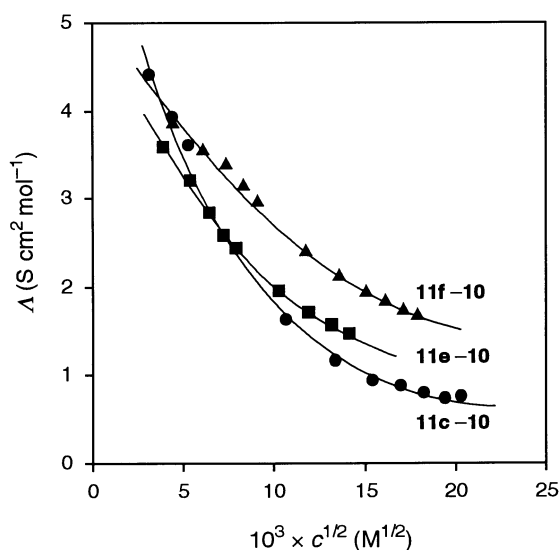


Figure 1. Onsager's plot for $11c-10$, $11e-10$, and $11f-10$ in DMSO at 25°C

Table 1. Limiting molar conductivities of ions and salts in DMSO at 25°C^a

Salt or ion	Λ_0 (S cm ² mol ⁻¹)
H ⁺	14.6 ^b
ClO ₄ ⁻	24.52 ^c
H ⁺ 10 ⁻	19.9
11c ⁺ ClO ₄ ⁻	38.8
11e ⁺ ClO ₄ ⁻	34.8
11f ⁺ ClO ₄ ⁻	34.7
14 ⁺ ClO ₄ ⁻	36.5
15 ⁺ ClO ₄ ⁻	30.2
14 ⁺ 10 ⁻	18.2 (17.3 ^d)
15 ⁺ 10 ⁻	10.9 (11.0 ^d)

^a Refs 15 and 26.

^b Ref. 42.

^c Ref. 43.

^d Sum of the limiting molar conductivities of component ions.

Table 2. Free energies of carbon–carbon bond heterolysis of ionically dissociative hydrocarbons and related compounds at 25 °C^a

Compound	Solvent	K_{het}° (10^{-6}M)	$\Delta G_{\text{het}}^{\circ}$ (kcal mol ⁻¹)
11a–10^b	DMSO	0.45	8.7
11b–10^b	DMSO	0.99	8.2
11c–10	DMSO	0.84	8.3
11d–10^b	DMSO	1.0	8.2
	Sulfolane ^c	0.16	9.3
11e–10	DMSO	1.0	8.2
	Sulfolane ^c	0.18	9.2
11f–10	DMSO	2.1	7.7
	Sulfolane ^c	1.3	8.0
11g–10^b	DMSO	6.4	7.1
	Sulfolane ^c	1.3	8.0
11h–10	DMSO	240	4.9
	Sulfolane ^c	11	6.8
11i–10	DMSO	140	5.2
	Sulfolane ^c	18	6.5
11j–10^b	DMSO	120	5.4
	Sulfolane ^c	19	6.5
13a–10	DMSO	49	5.9
13b–10	DMSO	93	5.5
13c–10	DMSO	400	4.6
13d–10	DMSO	280	4.8
13e⁺10⁻	DMSO	460	4.6
13f⁺10⁻	DMSO	410	4.6
14⁺10⁻	DMSO	>1000 ^d	<4
	CH ₃ CN	210	4.8
	ClCH ₂ CH ₂ Cl	66	5.7
	CH ₂ Cl ₂	12	6.7
	THF	14	6.6
15⁺10⁻	DMSO	>1000 ^d	<4
16⁺10⁻	DMSO	>1000 ^d	<4
17⁺10⁻	DMSO	>1000 ^d	<4
18⁺10⁻	DMSO	>1000 ^d	<4
11c–12	DMSO–CS ₂ (4:1, v/v)	0.14	9.3
11f–12	DMSO–CS ₂ (4:1, v/v)	1.0	8.2
11h–12	DMSO–CS ₂ (4:1, v/v)	2.2	7.7
13e–12^e	DMSO–CS ₂ (4:1, v/v)	29	6.2
14–12	DMSO–CS ₂ (4:1, v/v)	>1000 ^d	<4
15⁺12⁻	DMSO–CS ₂ (4:1, v/v)	>1000 ^d	<4

^a Refs 15, 18, 20 and 26.^b Mixture of two positional isomers.^c Contains 5% (v/v) of 3-methylsulfolane to prevent freezing.^d Equilibrium constant could not be determined due to essentially complete dissociation (>99%).^e Mixture of diastereomers.

carbon bond heterolysis of hydrocarbons. For the precise determination of equilibrium constants from the spectro-

Table 3. Enthalpies and entropies of carbon–carbon bond heterolysis in DMSO^a

Compound	$\Delta H_{\text{het}}^{\circ}$ ^b (kcal mol ⁻¹)	$\Delta S_{\text{het}}^{\circ}$ (cal K ⁻¹ mol ⁻¹)
11c–10	3.1 (19.6)	-17
13a–10	-0.32	-20
13b–10	-0.81 (11.9)	-20
13d–10	-0.38	-19

^a Refs 15 and 20.^b Values predicted from Arnett's equations in parentheses.

photometrically measured concentrations of generated ions, the degree of dissociation, α , has to be in the range 0.001–0.99. Fortunately, the degrees of ionic dissociation of most of the hydrocarbons described above in solvents such as DMSO and sulfolane lie in this range, except for the salts **14⁺10⁻**, **15⁺10⁻**, **16⁺10⁻**, **17⁺10⁻**, **18⁺10⁻** and **15⁺12⁻**, for which no covalent bond formation could be detected ($\alpha > 0.99$). The free energies of heterolysis, $\Delta G_{\text{het}}^{\circ}$, were then obtained from the equilibrium constants. The results are summarized in Table 2. The enthalpies and entropies of heterolysis were also determined for some hydrocarbons from the temperature dependence of the equilibrium constants (Table 3).

As discussed below, the thermodynamic parameters

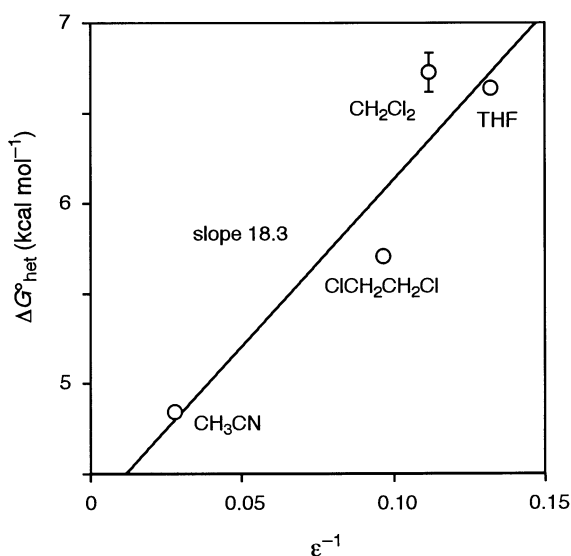


Figure 2. Born plot for heterolysis of **14–10** in various solvents at 25°C

obtained here demonstrate the importance of three factors, namely, solvent, electronic and steric effects, in controlling the energy of heterolysis.

Solvent effects

The dissociation behavior in various solvents was examined using the salt **14**⁺**10**[−].²⁶ When dissolved in benzene, chloroform or carbon tetrachloride, this salt, a green solid, is completely converted into the covalent form **14–10**, giving a brown solution. In acetonitrile, 1,2-dichloroethane, dichloromethane and THF, the ionic and covalent forms co-exist, in equilibrium. As already mentioned, essentially complete dissociation was observed in DMSO. Thus, a full change in degree of dissociation over the entire spectrophotometrically observable range can be observed by simply altering the solvent polarity. A linear relationship was obtained between the free energies for ionization and the reciprocal of the solvent dielectric constant (Fig. 2). The linear relationship, predicted from the Born equation, indicates that simple electrostatic solvation of ions is one of the major controlling factors for carbon–carbon heterolysis. Linear relationships between $\Delta G^\circ_{\text{het}}$ and ϵ^{-1} have also been reported for the cyclopropenylum ion–arylmalononitrile system (Scheme 5; $R_1 = \text{Me, Ph}$; $R_2 = \text{NO}_2$) by Arnett and co-workers^{10,34}.

Interestingly, the covalent molecule **14–10** in chloroform was immediately converted into the salt form **14**⁺**10**[−] when the chloroform was evaporated, leaving a dark-green residue. Alternatively, the salt was precipitated by cooling a chloroform solution of **14–10** at -78°C . Hence **14–10** is an unusual hydrocarbon that can exist only in solution. This seemingly strange behavior

Table 4. pK_{R^+} values and reduction potentials of carbocations.

Cation	pK_{R^+} ^a	E_{red} (V) ^b
11a ⁺	3.25	
11b ⁺	3.88	
11c ⁺	3.88	−0.510
11d ⁺	4.57	−0.61
11e ⁺	4.90	−0.695
11f ⁺	5.42	−0.720
11g ⁺	5.76	−0.640
11h ⁺	7.63	−0.760
11i ⁺	7.80 ^c	−0.762 ^c
11j ⁺	7.80 ^c	−0.765 ^c
13a ⁺		−1.412 ^d
13b ⁺	7.09 ^e	−1.525 ^d
13c ⁺		−1.532 ^d
13d ⁺		−1.566 ^d
13e ⁺	7.29 ^d	−1.583 ^d
13f ⁺		−1.632 ^d
14 ⁺	10.0	−2.20
15 ⁺	13.6 ^f	−1.42 ^g
16 ⁺	8.9	−1.48
17 ⁺	8.72	−0.856
18 ⁺	13.0 ^h	−1.120 ^h

^a In 50% aqueous acetonitrile; Ref. 13.

^b CV peak potential vs Ag/Ag⁺ measured in acetonitrile; Ref. 13.

^c Ref. 44.

^d Ref. 20.

^e Ref. 31.

^f Ref. 25.

^g Ref. 26.

^h Ref. 29.

may be understood by interpreting it as reflecting some relief of intermolecular steric congestion in the crystal lattice by ionization.^{26,27}

Free energies of heterolysis, shown in Table 2, indicate that the dissociation is much more favored in DMSO than in sulfolane, in spite of the magnitude of the dielectric constants (46.68 and 43.3, respectively), which are nearly identical with each other. However, the former has a much greater donor number than the latter (29.8 and 14.8, respectively³⁵). Therefore, the low dissociation energy observed in DMSO can be ascribed to the strong basic coordination tendency of this solvent, leading to effective stabilization of the ionized form. The strong solvation by DMSO also explains the large negative $\Delta S^\circ_{\text{het}}$ values listed in Table 3.

Free energy of heterolysis vs thermodynamic stability of generating ions—electronic effects

It would be interesting to determine the relationship between the free energies of heterolysis and the stabilities of the ions formed. The pK_{R^+} value, which is defined based on carbon–oxygen heterolysis, is a well known measure of thermodynamic stability of carbocations (Table 4). The $\Delta G^\circ_{\text{het}}$ for the carbon–carbon bond is linearly related to $-2.303RT \times pK_{R^+}$ with a slope of 0.65

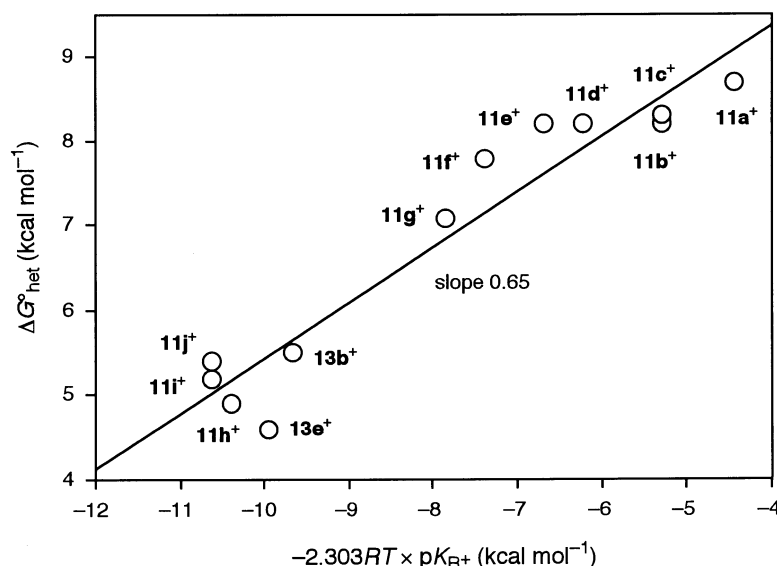


Figure 3. Plot of $\Delta G_{\text{het}}^{\circ}$ in DMSO for ionically dissociative hydrocarbons having the anionic moiety 10^{-} against $-2.303RT \times pK_{R^{+}}$. The $pK_{R^{+}}$ values were taken from Table 4. The numbers indicate the structure of the carbocation formed by the dissociation of C—C and C—O bonds

(Fig. 3). The linear relationship implies that the two types of covalent bonds, C—C and C—O, are closely related with regard to heterolysis and ion combination. It is not clear why the sensitivity of the C—C bond is lower than that of C—O, although possible explanations include the difference in the strength of these bonds and that in the solvent in which the heterolysis was studied.

While it is of great interest to examine precisely the influence of the thermodynamic stability of ions on covalent and ionic bond formation, an increase in bulkiness often accompanies an increase in electronic

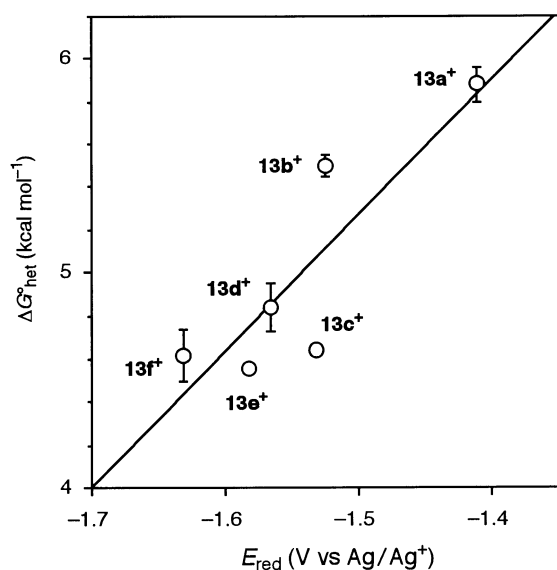


Figure 4. A Plot of $\Delta G_{\text{het}}^{\circ}$ for (13a-f)-10 determined in DMSO at 25°C against E_{red} of $13a-f^{+}$. The E_{red} values were taken from Table 4

stability, making it difficult to examine the electronic effect alone, separately from the steric effect. 1-Aryl-2,3-dicyclopropylcyclopropenylium ions, $13a-f^{+}$, permit a progressive change in electronic stability by changing the substituent on the aryl group, while the steric factor near the cationic center remains essentially unchanged.²⁰ Since the coordination of these cations with 10^{-} occurs exclusively at the cyclopropenylium ring carbon on which the cyclopropyl group is connected (*cf.* Scheme 9), the aryl group is located at a position where the steric effect of the *para* or *meta* substituent is unimportant. Unfortunately, $pK_{R^{+}}$ values are not available in the literature for most of cations $13a-f^{+}$. Reduction potentials, E_{red} , however, can be used as an alternative measure of cation stability, and these can be determined precisely and conveniently by cyclic voltammetry. It has been reported that the reduction peak potentials of substituted cyclopropenylium ions show a linear correlation with their $pK_{R^{+}}$ values.¹³ As can be seen in Fig. 4 the plot of $\Delta G_{\text{het}}^{\circ}$ against E_{red} of the cationic moiety showed a general tendency that heterolysis becomes less endergonic as the generating cation becomes more stabilized.

It should be noted that the E_{red} values of carbocations listed in Table 4 are much more negative than the oxidation potentials (vs Ag/Ag^{+}) of 10^{-} (-0.18 V in acetonitrile)³⁶ and 12^{-} (-0.25 V in DMSO).^{1,16} This indicates that the ion pairs are more stable than the corresponding radical pairs, which is in accord with heterolysis being the preferred reaction, rather than homolysis.

The influence of a slight change in the electronic stability of cations can be more pronounced in the solid-state molecular structure, which will be discussed later.

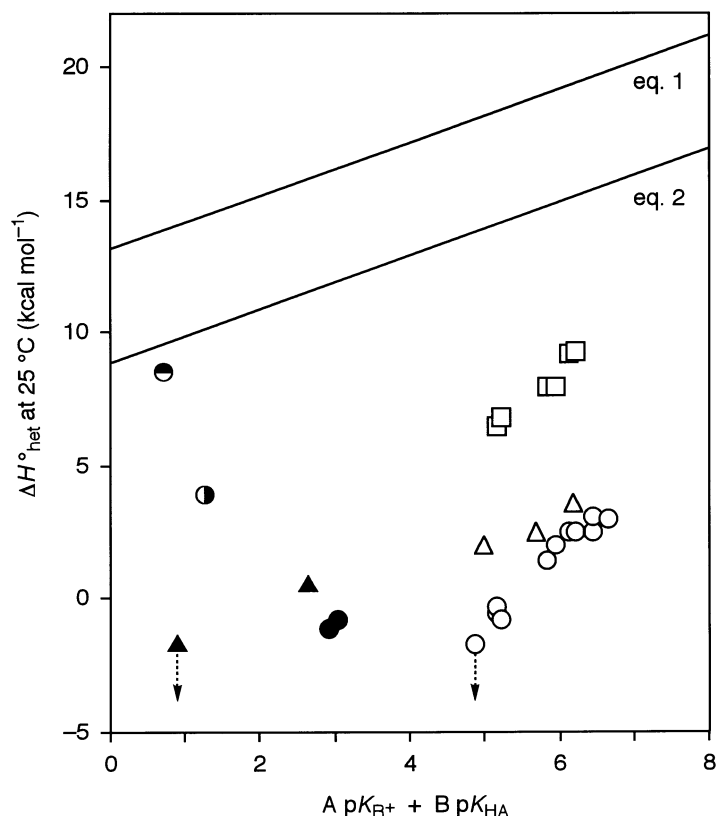


Figure 5. Plot of $\Delta H_{\text{het}}^{\circ}$ against Arnett's equation scale. $\Delta H_{\text{het}}^{\circ}$ values were taken from Table 3 or calculated from the $\Delta G_{\text{het}}^{\circ}$ values listed in Table 2, assuming that the $\Delta S_{\text{het}}^{\circ}$'s are $0 \text{ cal K}^{-1} \text{ mol}^{-1}$ in sulfolane and acetonitrile and $-19 \text{ cal K}^{-1} \text{ mol}^{-1}$ in DMSO and DMSO- CS_2 (4:1, v/v). Points with a downward arrow indicate the upper limit for $\Delta H_{\text{het}}^{\circ}$. \circ : (11a-j)-10 and 17-10 in DMSO; \bullet : (13b,e)-10 in DMSO; \square : (11d-j)-10 in sulfolane; \triangle : (11c,f,h)-12 in DMSO- CS_2 (4:1, v/v); \blacktriangle : 13e-12 and 14-12 in DMSO- CS_2 (4:1, v/v); \ominus , 20 in acetonitrile; \oplus , 9 ($R_1 = \text{Me}$, $R_2 = \text{H}$) in acetonitrile

Steric assistance

The third factor to be examined, the steric effect, is known to play an important role in determining the free energy of carbon-carbon homolysis.³⁷⁻³⁹ Rüchardt and co-workers³⁹ investigated the products and kinetics of thermolysis for a large number of highly branched aliphatic hydrocarbons and phenyl- or cyano-substituted derivatives, and have shown quantitatively that, in addition to stability of radicals, the steric congestion in a dissociating molecule is a major enhancing factor in the homolytic cleavage of carbon-carbon σ bonds.

Arnett and co-workers proposed,⁴⁰ as one of the results of their systematic studies on carbon-carbon bond formation through the reaction of carbocations and carbanions, empirical relationships (master equations) that correlate, with high precision, the heat of heterolysis (ΔH_{het}) with the thermodynamic stabilities of cations ($\text{p}K_{\text{R}^+}$) and anions ($\text{p}K_{\text{HA}}$). From the results of calorimetry for the coordination of resonance-stabilized carbocations and carbanions in sulfolane or acetonitrile over a wide range of ion stability, they demonstrated that equation (1) or (2), depending on the class of the generating carbocation, predicts heats of heterolysis of

carbon-carbon σ bonds. However, it was not certain that these equations can be extended to the present systems, since they had been derived from data for sterically unencumbered ions.

For secondary cations:

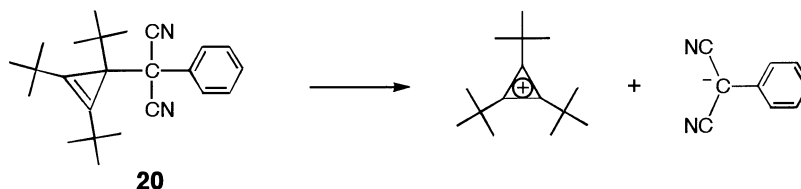
$$\Delta H_{\text{het}} = 13.18 - 0.324(\text{p}K_{\text{R}^+}) + 1.307(\text{p}K_{\text{HA}}) \quad (1)$$

For tertiary cations:

$$\Delta H_{\text{het}} = 8.895 - 0.648(\text{p}K_{\text{R}^+}) + 1.294(\text{p}K_{\text{HA}}) \quad (2)$$

The fact that the expression of ΔH_{het} is separated into two equations is understood in terms of the difference in steric hindrance for secondary and tertiary cations. That is, equation (1) implicitly includes the steric term which is common to the cation-anion coordination of 'normal' secondary cations, whereas equation (2) includes that of 'normal' tertiary cations. If there is additional steric congestion, caused by bulky substituents in the vicinity of the ion center, a negative deviation from these linear relations would be expected.

To assess the specific steric factor controlling the heterolysis by equations (1) and (2), $\Delta G_{\text{het}}^{\circ}$ must be converted into $\Delta H_{\text{het}}^{\circ}$. The entropies of heterolysis, $\Delta S_{\text{het}}^{\circ}$ for the cyclopropenylum ion-malononitrile anion



Scheme 11

system shown in Scheme 5 have been reported to be near zero, and hence $\Delta H_{\text{het}}^{\circ} \approx \Delta G_{\text{het}}^{\circ}$, in acetonitrile. It may be reasonable to assume that the values for $\Delta H_{\text{het}}^{\circ}$ and $\Delta G_{\text{het}}^{\circ}$ are also apparently close to each other in sulfolane, since the dielectric constant (43.3) and the donor number (14.8³⁵) of this solvent are close to those of acetonitrile (37.5 and 14.1,³⁵ respectively). In DMSO, on the other hand, large negative $\Delta S_{\text{het}}^{\circ}$ values were observed for hydrocarbons listed in Table 3, owing to strong solvation of the carbocation. If one assumes that $\Delta S_{\text{het}}^{\circ}$ is constant at *ca* $-19 \text{ cal K}^{-1} \text{ mol}^{-1}$ throughout the present systems, then the $\Delta H_{\text{het}}^{\circ}$ values are estimated to be smaller by *ca* 6 kcal mol^{-1} than $\Delta G_{\text{het}}^{\circ}$ in this solvent.

For a comparison of Arnett's equations and the $\Delta H_{\text{het}}^{\circ}$ values of our systems, equation (1) should be employed for compounds of which the cationic component is **11** and equation (2) for those containing **13** or **14** as the cationic component. As shown in Fig. 5 the $\Delta H_{\text{het}}^{\circ}$ values of these compounds are 10–20 kcal mol^{-1} lower than predicted from Arnett's equations. The large negative deviations from the equations are explained by the steric congestion in the present systems, although the high donating ability of DMSO may also contribute to the lowering of $\Delta H_{\text{het}}^{\circ}$.

A similar deviation arising from the steric effect was observed for the heterolysis of the crowded compound **20** into the tri-*tert*-butylcyclopropenylium ion ($\text{p}K_{\text{R}^+} = 6.6$) and the phenylmalononitrile anion ($\text{p}K_{\text{HA}} = 4.24$) in acetonitrile (Scheme 11).¹⁵ The $\Delta H_{\text{het}}^{\circ}$ value, $3.9 \text{ kcal mol}^{-1}$ (again obtained by assuming that $\Delta S_{\text{het}}^{\circ}$ is close to zero), is about $6.3 \text{ kcal mol}^{-1}$ smaller than expected from equation (2), whereas the deviation is only $1.1 \text{ kcal mol}^{-1}$ for (trimethylcyclopropen-1-yl)phenylmalononitrile (**9**, $\text{R}_1 = \text{Me}$, $\text{R}_2 = \text{H}$; see Scheme 5), which dissociates into the less hindered trimethylcyclopropenylium ion ($\text{p}K_{\text{R}^+} = 7.4$) and phenylmalononitrile anion (observed $\Delta H_{\text{het}}^{\circ} = 8.5 \text{ kcal mol}^{-1}$; predicted $\Delta H_{\text{het}}^{\circ} = 9.59 \text{ kcal mol}^{-1}$).³⁴

It also turned out that the steric repulsion between ions also plays an important role in the formation of hydrocarbon salts. Although the high stabilities of the component ions are a primary requirement for the prevention of covalent bond formation, Arnett's equations predict that the coordination of **13e**⁺ and **14**⁺–**18**⁺ with **10**[−] and that of **14**⁺ and **15**⁺ with **12**[−] (from which salts were obtained) are still energetically favorable by 7–

18 kcal mol^{-1} . The concomitant increase in stability and that in steric effect often occurs, since the introduction of an ion-stabilizing substituent usually results in significant steric hindrance. Therefore, the formation of the salts is also assisted by a high degree of steric repulsion between the component ions.

Borderline cases. Exceedingly easy switching of carbon–carbon bonds in the solid state

As mentioned before, the steric requirement for covalent bond formation is nearly constant for 1-aryl-2,3-dicyclopropylcyclopropenylium ions **13a-f**⁺, and hence their reactions with **10**[−] are essentially controlled solely by electronic effects. Therefore, these cations are ideal for studying the influence of a gradual change in cation stability by changing the substituent on the aromatic ring. Despite the similar thermodynamic stabilities of **13a-f**⁺, the solid products obtained by combination with **10**[−] were distinguishable: cations **13a-d**⁺ gave coordination products (**13a-d**)–**10**, whereas carbocation–carbanion salts **13e**⁺**10**[−] and **13f**⁺**10**[−] were obtained from cations **13e**⁺ and **13f**⁺.^{19,20} It is apparent that from the reduction potentials of **13a-f**⁺ (Table 4) the product of the reaction with **10**[−] suddenly changes from a covalent compound to a salt as the stability of the cation moiety is gradually increased. The borderline between the two types of reactions lies between **13d**⁺ and **13e**⁺. The small difference (0.017 V) in the E_{red} values of these cations suggests that only a slight difference ($0.4 \text{ kcal mol}^{-1}$ or less) in electronic stability can completely alter the type of bond. The absence of a marked difference in $\Delta G_{\text{het}}^{\circ}$ between (**13a-d**)–**10** and (**13e,f**)–**10** (Table 2) suggests that a certain solid-state property is concerned with the abrupt switching of the crystalline form upon changing the substituent. Presumably, the balance between the energy of heterolysis of the carbon–carbon σ bond and the lattice energy in the salt form determines the product.

There might be a possibility that an extraneous mechanical energy also causes the interconversion between the two forms. Indeed, the orange solid **13b**–**10** partially heterolyzed to give a green color when pulverized in a vibrating ball-mill, exhibiting piezochromism.²⁰

It is also noteworthy that, whereas **13e**⁺**10**[−] was obtained as a solid by reprecipitation from THF solution

with added acetonitrile or by evaporation of a DMSO solution, the covalent form **13e-10** was obtained when the solvent was evaporated from a dichloromethane solution. NMR spectra, measured in CDCl_3 , demonstrated that the solids formed from DMSO and dichloromethane solutions contained 2.6 and 0.15 molar equivalents, respectively, of solvent molecules.³³ This is another example of a facile change in the nature of carbon-carbon bonds induced by a small change in the molecular environment.

CONCLUSION

The hydrocarbons reported here are exceptional in the sense that they undergo heterolytic dissociation into a carbocation and a carbanion through heterolysis of a carbon-carbon σ bond. The success in the preparation of these hydrocarbons is based on developments in the field of highly stabilized carbocation and carbanion chemistry. The tropylium ion, the first non-benzenoid aromatic ion, was synthesized as the bromide salt, **11c**⁺Br⁻, by Doering and Knox⁴¹ in 1954. It was 13 years later that Kuhn and Rewicki^{12a} reported the synthesis of a hydrocarbon anion, **10**⁻, which has unusually high stability. A further 18 years, however, were required before an experiment was carried out in which these ions were simply combined to build up a hydrocarbon of a novel class, **11c-10**.¹¹ Structural changes in the cationic and anionic moieties allowed the syntheses of a series of ionically dissociative hydrocarbons which show different propensities toward heterolysis. Furthermore, it was demonstrated that, in extreme cases, some hydrocarbons can be isolated as ionic solids—an advance in diminishing the distance between organic and inorganic chemistry.

The reversible (or complete, in some cases) ionization of the hydrocarbons was investigated by means of spectrophotometry and electrical conductivity measurements. The study of thermodynamics for reversible heterolysis revealed several factors that control the free energy of heterolysis. First, the importance of ion stability, which is influenced by solvation and molecular structure, was effectively shown by the linear free energy relationship between $\Delta G_{\text{het}}^\circ$ and suitable energy terms such as ϵ^{-1} , $\text{p}K_{\text{R}^+}$ and E_{red} . Second, the destabilization of the starting molecule by steric congestion, which is released by dissociation, is another driving force for the heterolysis of the hydrocarbons examined in this work. The magnitude of steric assistance has been evaluated by comparing the observed $\Delta H_{\text{het}}^\circ$ values with those predicted by Arnett's empirical equations.

Further subjects for future investigations include the study of kinetic properties. It is of particular interest to examine the transition state structure, *i.e.* an ion pair or a radical pair, connected by a partially broken bond. Although solvation is one of the principal controlling

factors for heterolysis, the issue of whether the thermal motion of solvent molecules follows the bond breaking so precisely that effective solvation is maintained en route to the transition state is in question. A determination of activation parameters is under way, in order to obtain information as to how much ionic character has been developed at the transition state.

Acknowledgments

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