

150. Homopolar and Heteropolar Bond Dissociation Energies and Heats of Formation of Radicals and Ions in the Gas Phase II. The Relationship between Structure and Bond Dissociation in Organic Molecules

by Kurt W. Egger and Alan T. Cocks¹⁾

Monsanto Research S.A., Eggbühlstrasse 36, 8050 Zürich

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Summary. The preceding paper presents a critical tabular compilation of 2-center homo- and heteropolar bond dissociation energies. This paper deals with some empirically derived general aspects of these data, particularly regarding relationships between structure and reactivity, *i.e.* substituent effects on bond dissociation energies. 'Extra' stabilization energies generated in electronically delocalized radicals or ions derived from these experimental data are also presented.

I. Introduction

A. General. – A critical evaluation and compilation of the available heteropolar (D^*H°) and homopolar (DH°) bond dissociation energies (BDE) and the corresponding heats of formation (ΔH_f°) of radicals and ions is presented in the preceding paper [1]. The present paper deals with some interesting general aspects and apparent trends that can be derived from these data, whereby the relationship between structure and bond dissociation energies, is of course, of primary interest. Such empirically derived relationships are often quite useful for *a priori* predictions of DH° , D^*H° or ΔH_f° of molecules radicals and ions, where no experimental data are available. The consistencies and trends in the observed data [1] also demonstrate the need for theoretical quantitative description of chemical bonding.

In Section II of this paper the general relationships between structure and bond dissociation energies (listed in tables 2 to 5 of reference [1]) are discussed. Some particular aspects such as 'substituent effects' or 'extra stabilization energies' in delocalized radicals etc. will be presented in chapter III. All bond dissociation energies refer to 25°C and 1 atm. pressure. DH_{298}° stands for homopolar, $D^*H_{298}^\circ$ for heteropolar bond dissociation energies defined as



$$DH_{298}^\circ(\text{R-X}) = \Delta H_{298}^\circ(1) = \Delta H_{f,298}^\circ(\text{R}^\cdot) + \Delta H_{f,298}^\circ(\text{X}^\cdot) - \Delta H_{f,298}^\circ(\text{R-X})$$

$$D^*H_{298}^\circ(\text{R-X}) = \Delta H_{298}^\circ(2) = \Delta H_{f,298}^\circ(\text{R}^+) + \Delta H_{f,298}^\circ(\text{X}^-) - \Delta H_{f,298}^\circ(\text{R-X})$$

¹⁾ Post-doctoral Research associate, present address: Department of Chemical Engineering, University College, London WC1E, 7 J. E.

For experimental details and the definition and use of symbols the reader is referred to the preceding paper [1]. Throughout this paper energies are given in kcal mol⁻¹ 2).

II. Discussion of the Experimental Data on Bond Dissociation Energies

A. Dissociation Energies of (Alkyl)-X Bonds (Table 2, Ref. [1]).

The bond dissociation energies are generally reduced with increasing substitution on one or both of the bond breaking centers.

The alkyl substituent effects are evidently much larger for hetero- than for homopolar bond breakage. For hydrocarbons the ratio of $D^*H_{298}^{\circ}(\text{R}-\text{CH}_3)/DH_{298}^{\circ}(\text{R}-\text{CH}_3)$ decreases in the series $\text{R} = \text{CH}_3-$, C_2H_5- , $i\text{-C}_3\text{H}_7-$ and $t\text{-C}_4\text{H}_9$ from 3.6 to 3.3, 3.1 and 3.0 respectively.

For compounds other than hydrocarbons the following $D^*H_{298}^{\circ}(\text{R}-\text{X})/DH_{298}^{\circ}(\text{R}-\text{X})$ ratios are obtained:

Table 1. $D^*H_{298}^{\circ}(\text{R}-\text{X})/DH_{298}^{\circ}(\text{R}-\text{X})$ for R-X bonds where R equals alkyl groups

R-X	F	Cl	Br	I	OH	OCH ₃	NH ₂	NO	NO ₂
CH ₃	2.4	2.7	3.1	3.8	3.0	3.4	3.4	6.6	3.8
C ₂ H ₅	2.1	2.4	2.7	3.3	2.7	3.0	3.1	6.1	3.4
<i>i</i> -C ₃ H ₇	1.9	2.1	2.4	2.9	2.4	2.7	2.8	5.7	3.0
<i>t</i> -C ₄ H ₉	1.7	2.0	2.3	2.8	2.3	2.6	2.7	5.4	2.8

The systematic trend observed in these data, demonstrates the consistency of the experimental values and is primarily a consequence of the differences in ground state polarity of the bonds with respect to homopolar bond breakage. For heteropolar bond breakage into carbonium ions and X⁻ anions the effective amount of the alkyl stabilization energy remains essentially constant. Viewed within the concept of the relative ionic character of the bonds and a stabilizing effect *via* alkyl group polarizability the observed trends in the ratios are within expectation and overall systematic. The high values for the D^*H°/DH° ratios for the C-NO bonds, resulting from the low homopolar BDE's, are remarkable.

The homopolar bond dissociation energies of cyclopropyl-X and cyclobutyl-X are larger than those for isopropyl-X. This reflects the decreasing effect of 'strain' energy (in terms of 'bent' bonds) in the series C=C-H(108 kcal mol⁻¹) cyclopropyl - H(101), cyclobutyl - H(96.5), cyclohexyl - H(95) and isopropyl - H(95) [2]. The lower values for $DH_{298}^{\circ}(\text{cyclopentyl} - \text{H})$ and $DH_{298}^{\circ}(\text{cycloheptyl} - \text{H})$ compared with cyclohexane appear to be real and have been interpreted as reflecting differences in H-H interactions and torsional strains between parent molecule and radical formed [2].

The heteropolar $D^*H_{298}^{\circ}$ for C₂ to C₆ cycloalkyl-X follow the same general trend observed for the homopolar bond dissociation energies with the apparent exception of cyclobutyl-X. The only experimental value for $\Delta H_f^{\circ}(\text{cyclo-C}_4\text{H}_7^{\dagger}) \approx (214)$ [3] appears to be about 6 kcal mol⁻¹ too low and a value of 220 is suggested. This is in perfect agreement with the value of 221 kcal mol⁻¹ for the isomeric cyclo-C₃⁺H₄CH₃ and the observations of common mass spectral decomposition paths for the two

2) 1 kcal mol⁻¹ = 4.186 kJ mol⁻¹.

(C₄H₇)⁺ isomers [4] and a calculated (CNDO) difference in heats of formation of ~ 1 kcal mol⁻¹ [5] between the two isomers cyclo-C₄H₇⁺ and cyclo-C₃⁺H₄CH₃.

Even for the lowest heteropolar D*H₂₉₈^o of ~ 140 kcal mol⁻¹ observed for *t*-butyl-I, a temperature > 10,000 K is required to produce a thermally induced homogeneous heteropolar bond breakage that would amount to 10% of the homopolar bond breakage. It is then evident, that thermal heteropolar bond breakage never competes with homopolar bond breakage at feasible temperatures. Gas phase reactions which show a distinct homogeneous heteropolar component, must then involve a concerted multi-center bond breakage [6].

By analogy with the parent molecules the heats of formation of *n*-alkyl radicals can be calculated from the ethyl radical, adding -4.95 kcal mol⁻¹ per additional -CH₂ group. For linear carbonium ions a similar incremental behaviour is not apparent from the literature data [3]: C₂H₅⁺ (219), *n*-C₃H₇⁺ (208), *n*-C₄H₉⁺ (218), *n*-C₅H₁₁⁺ (171) and *n*-C₆H₁₃⁺ (170). This is probably largely due to the uncertainties attached to the data. It is also possible that some of the inconsistencies in these data at least in part, reflect changes in the structure of the ions.

Another interesting aspect of the heteropolar dissociation energies of R-X bonds (R = alkyl) is the fact, that D*H₂₉₈^o(R-CH₃) in general equals or exceeds D*H₂₉₈^o(R-H) by a few kcal mol⁻¹ in contrast to homopolar bond breakage. This observation holds for all the pertinent experimental data listed in ref. [1]. This is to be expected based on the fact that $\Delta H_f^o(\text{H}^-) \approx \Delta H_f^o(\text{CH}_3^-)$ and consequently D*H₂₉₈^o(R-CH₃) - D*H₂₉₈^o(R-H) $\approx \Delta H_f^o(\text{R-CH}_3) - \Delta H_f^o(\text{R-H})$. As examples $\Delta H_f^o(\text{H}_2) - \Delta H_f^o(\text{CH}_4) = 17.9$ and D*H₂₉₈^o(CH₃-H) - D*H₂₉₈^o(H-H) ≈ 17 compared to $\Delta H_f^o(\text{C}_2\text{H}_5-\text{CH}_3) - \Delta H_f^o(\text{C}_2\text{H}_5-\text{H}) = 4.6$ and D*H₂₉₈^o(C₂H₅-CH₃) - D*H₂₉₈^o(C₂H₅-H) = 4 kcal mol⁻¹. In general it can be concluded that D*H₂₉₈^o(R-C) > D*H₂₉₈^o(R-H) except where the carbanion formed is stabilized as is the case with phenylanions: (D*H₂₉₈^o(H-H) = 401 and D*H₂₉₈^o(H-C₆H₅) = 387), or is to be expected for higher alkylated carbanions like isopropyl⁻ or *t*-butyl⁻ for which reliable data on electron affinities are not yet available.

Comparing the *homopolar* bond dissociation energies for alkanes reveals a very interesting 'isomeric' substituent effect. Below are listed differences in DH₂₉₈^o(R₃C_a-C_bR₃) (where R is an alkyl- or H-group) for various isomer pairs.

Isomer Pair	$\Delta DH_{298}^o(\text{R}_3\text{C}_a-\text{C}_b\text{R}_3)$ in kcal mol ⁻¹
(CH ₃) ₂ CH-CH ₃ /CH ₃ CH ₂ CH ₂ -CH ₃	1
(CH ₃) ₂ CH-CH ₂ CH ₃ /CH ₃ CH ₂ CH ₂ -CH ₂ CH ₃	1.2
(CH ₃) ₂ CH-CH(CH ₃) ₂ /CH ₃ CH ₂ CH ₂ -CH(CH ₃) ₂	2.2
(CH ₃) ₂ CH-C(CH ₃) ₃ /CH ₃ CH ₂ CH ₂ -C(CH ₃) ₃	3.3

In all four sets of isomers an *n*-propyl center on carbon atom C_a is changed to an isopropyl center. On carbon center C_b hydrogen atoms are stepwise replaced by methyl substituents. A priori one might expect the same difference for all the isomer pairs. There appears to be a pronounced 'steric' influence³⁾ on the alkyl substituent effect


³⁾ A very pronounced steric effect on the C-C bond strength in alkanes has been reported for hexaethylethane [35] and hexacyclopropylethane [36] with DH^o's more than 20 kcal mol⁻¹ weaker than DH^o ((CH₃)₃C-C(CH₃)₃).

at least in the case of R_3C-CR_3 bond breaking. This 'steric' influence deserves particular attention in any attempts to arrive at a quantitative description of chemical bonding.





Viewed within the concept of the periodic table, the H-X bond dissociation energies appear to be consistent.




H-X	H-CH ₃	H-NH ₂	H-OH	H-F
$DH_{298}^{\circ}(\text{HX})$	104	110	119	136
$D^*H_{298}(\text{HX})$	418	407	390	370

B. Dissociation Energies of RC-X Bonds in Vinyl, Allyl, Benzyl- and Phenyl-type Compounds. (Table 3, Ref. [1]).

The strengths of $>C=C-X$ type bonds are generally about 10 kcal mol⁻¹ and those of -X bonds 15 kcal mol⁻¹ larger than those for the corresponding saturated hydrocarbons.

The strengths of $>C=C-C-X$ type bonds are reduced by the 'extra stabilization energies generated in the electronically delocalized 'allyl'-type radicals and ions. For details compare section III.

Values for , , , and  which are not given in ref. [1] can be assumed to equal the BDE for C=C-X. There are not enough data available on the α -alkyl substituent effect for $C=C^R-X$ bonds.

As would be predicted, the highest 'olefinic' BDE's listed in reference [1] are those for -X bonds, *i.e.* -F for homopolar and -H for heteropolar breakage. The lowest heteropolar bond strength (102 kcal mol⁻¹) is that for 7-cycloheptatrienyl-I, due to the 'aromatic' nature of the product ion cyclo-C₇H₇⁺. The lowest homopolar DH° 's are those, calculated for cyclohexadienyl-NO bonds, which would only be stable at sub-ambient temperatures.

The ratio of hetero to homopolar bond strengths again shows the same general trend and very similar values to those observed for the corresponding saturated compounds, which have been discussed in the previous section.

M- and p-substituents appear to decrease the heteropolar D^*H° 's by a few kcal mol⁻¹.

C. Dissociation Energies of R-X Bonds where R contains Oxygen. (Table 4, Ref. [1]).

It is particularly noteworthy, that the homopolar and heteropolar $RC-\overset{\overset{O}{||}}{C}-H$ and $RC-\overset{\overset{O}{||}}{C}-X$ bonds are considerably weaker than the corresponding isoelectronic $RC-\overset{\overset{O}{||}}{C}-CH_2$ bonds. The same trend seems to hold also for $HC-\overset{\overset{O}{||}}{C}$ -halogen bonds. It appears, that the

difference in bond dissociation energies between $\text{RC}-\overset{\text{O}}{\parallel}{\text{X}}$ and $\text{RC}-\overset{\text{O}}{\parallel}{\text{CH}_2}$ bonds decreases with increasing 'ionic' character of the bond *i.e.* decreasing electron density on the carbonyl carbon atom, as can be seen from the data listed in *Table 2*.

Table 2. *Difference in the bond dissociation energies for the 'isoelectronic' bonds*

$$[DH_{298}^{\circ}(\text{HC}-\overset{\text{O}}{\parallel}{\text{X}})] - DH_{298}^{\circ}(\text{HC}-\overset{\text{O}}{\parallel}{\text{CH}_2}) = \Delta DH$$

X	H	CH ₃	C ₂ H ₅	<i>i</i> -C ₃ H ₇	<i>t</i> -C ₄ H ₉	F	Cl	Br	I	OH	OCH ₃
ΔDH_{298}°	21	14	14	13	15	(-3)	(5)	(7)	(11)	-9	-8
$\Delta D^*H_{298}^{\circ}$	26	15	-	-	-	(3)	(11)	(13)	(17)	-3	-3

It has been suggested [7], that the stabilization energy gained from the conjugation of the unpaired carbon electron in the $\text{RC}=\overset{\cdot}{\text{O}}$ radical with either one of the lone pair oxygen electrons is responsible for the lower homopolar $DH^{\circ}(\text{HC}-\overset{\text{O}}{\parallel}{\text{H}})$ compared to $DH^{\circ}(\text{HC}-\overset{\text{O}}{\parallel}{\text{H}})$. In terms of VB resonance structures this would imply a pre-dominance of $\text{HC}=\overset{\cdot}{\text{O}}$ type structures in the radicals formed. The apparent variations in the overall effect with the nature of the $\text{HC}-\overset{\text{O}}{\parallel}{\text{X}}$ bond (Table 2) as well as the fact, that similar effects can be derived for homopolar and heteropolar bond breakage would however not appear to be in accord with a simple concept of 'resonance' stabilization of the RC^{\cdot} radical when compared with $\text{RC}\overset{\cdot}{\text{C}}\text{H}_2$.

The fact, that DH° for $\text{RC}-\overset{\text{O}}{\parallel}{\text{OH}}$ and $\text{RC}-\overset{\text{O}}{\parallel}{\text{OCH}_3}$ bonds exceed even those for $\text{RC}-\overset{\text{O}}{\parallel}{\text{H}}$ and $\text{RC}-\overset{\text{O}}{\parallel}{\text{CH}_3}$ by about 9 kcal mol⁻¹ shows the conjugative stabilization of the CO₂-structure in these ground state molecules.

The R-substituent effects in the homopolar bond dissociation energies of $\text{RC}-\overset{\text{O}}{\parallel}{\text{X}}$ bonds are noticeably small. In the case of R = phenyl the homopolar DH° are lowered by 7 kcal for C-F, 2.4 for C-CH₃ and 0 for Ph-C- $\overset{\text{O}}{\parallel}{\text{H}}$ itself when compared to $\text{HC}-\overset{\text{O}}{\parallel}{\text{X}}$. The corresponding heteropolar bond dissociation energies are reduced by 37, 30 and 32 kcal mol⁻¹ respectively. Methyl-substituents have practically the same effect as phenyl-groups, demonstrating the *absence* of 'extra' stabilization, *i.e.* the absence of electronic delocalization via the phenyl radical moiety in $\text{C}_6\text{H}_5-\overset{\cdot}{\text{C}}=\overset{\text{O}}{\parallel}$. In the case of R = OH or OCH₃ the $\text{RC}-\overset{\text{O}}{\parallel}{\text{X}}$ bond dissociation energies appear to be significantly raised compared to $\text{HC}-\overset{\text{O}}{\parallel}{\text{X}}$.

Another interesting difference is that between $\text{CH}_3\text{O}-\text{H}$ and $\text{C}_6\text{H}_5\text{O}-\text{H}$. While the heteropolar bond dissociation energies, *i.e.* the acid strengths of both methanol and phenol are the same, the homopolar bond dissociation energies in phenol is 20 kcal lower, implying an 'extra' resonance stabilization energy in the $\text{C}_6\text{H}_5\text{O}^\cdot$ radical of about 20 kcal mol⁻¹ compared to 12 in $\text{C}_6\text{H}_5(\text{H}_2)$ (compare section III). This parallels the difference of 21 kcal mol⁻¹ in DH° between $(\text{CH}_3)_2\text{N}-\text{H}$ and $\text{C}_6\text{H}_5\text{N}-\text{H}$ [8].

The homopolar C-H bond strengths in alcohols are about the same as in the corresponding alkanes. The 'polarizability' – stabilization (compare section III) of alkyl groups and OH groups bonded to the reactive carbon center would then be about the same.

The ratios $D^*H_{298}^\circ(\text{R}-\text{X})/DH_{298}^\circ(\text{R}-\text{X})$ for oxygenated molecules are summarized in Table 3 below:

Table 3. $D^*H_{298}^\circ(\text{R}-\text{X})/DH_{298}^\circ(\text{R}-\text{X})$ for molecules containing oxygen atoms

R-X	H	CH ₃	F	Cl	Br	I	OH	OCH ₃	NH ₂
H ₃ C-C(H) ₂ -	2.8	3.3	2.1	2.4	2.7	3.3	2.7	3.0	3.1
H ₂ C=C(H)-	2.7	3.0	2.0	2.3	2.6	3.1	2.6	2.9	-
CH ₃ OC(H ₂)-	2.6	3.0	1.8	2.0	2.3	2.9	2.3	2.6	-
HOC(H ₂)-	2.7	3.1	2.0	2.2	2.5	3.0	2.4	2.6	-
H ₃ CO-	2.8	3.5					4.6	5.4	4.2
O=C(H)-	3.0	3.3	1.9	2.3	2.7	3.4	2.4	2.7	2.8
O=C(OH)-	3.5	3.9							

The higher D^*H°/DH° ratio's observed for O=C(OH)-X bonds when compared *e.g.* with $(\text{CH}_3)_2\text{C}(\text{H})-\text{X}$ are a consequence of the polar nature of the acids in the ground state. This is evident from the fact, that $\Delta H_f^\circ(\text{O}=\overset{\oplus}{\text{C}}(\text{OH})) \approx \Delta H_f^\circ((\text{CH}_3)_2\overset{\oplus}{\text{C}}(\text{H}))$. Heteropolar bond breakage resulting in a carbonium ion must then overcome the carbanion character in the ground state. The relatively high D^*H°/DH° ratios for peroxides and hydroperoxides on the other hand largely result from the particularly low homopolar peroxide bond dissociation energies.

A problem that has not yet been solved satisfactorily is that of the true value for the O=C(R)C(R₂)-X bonds, *i.e.* the value of the 'extra' stabilization in the O=C-C[·]-type radicals. For more details compare section III.

For the alcohol series the values for $DH_{298}^\circ(\text{R}_3\text{CO}-\text{H})$ are practically the same: 104.5 ± 1 kcal mol⁻¹ for methanol through to *t*-butanol. The same small next nearest neighbor substituent effect of alkyl groups is demonstrated with practically equal values for $DH^\circ(\text{HOC}(\text{H}_2))-\text{H}$ and $DH^\circ(\text{CH}_3\text{OC}(\text{H}_2))-\text{H}$.

D. Dissociation Energies of RC-X Bonds where R contains Halogen (Table 5, ref. [1]).

A large proportion of the BDE data of halogen compounds are uncertain as they are based on estimated values [9] due to the lack of reliable experimental data particularly on the heats of formation of the molecules.

In general the introduction of halogen bonded to the reactive carbon center has a relatively small effect on the C-X bond dissociation energies. In the case of Cl, Br,

and I the BDE's are usually either unaffected or then lowered with increasing substitution. For fluorine substituents a trend towards higher values is indicated. These effects are discussed in more detail in section III.

The D^*H^0/DH^0 ratio's observed for these bonds are perfectly in line with those discussed previously for other bonds.

III. Substituent Effects on the Strength of C-X Bonds

Considering the experimental error limits of ~ 1 kcal mol⁻¹ for homopolar DH^0 values, only α -substituents, *i.e.* substituents *directly* bonded to one of the two reactive centers involved in the bond breaking step, have a significant effect. With the exception of π -bonded systems of the type discussed in section III, β -substituents affect the homopolar bond strength in general to less than ~ 1 kcal mol⁻¹. Essentially the same is true for heteropolar BDE's even though a slight substituent effect appears to be indicated. (Compare next section). To a first approximation β -substituent effects can then be neglected.

Where large β -substituent effects are observed, they reflect a change in the nature of the fragment: for example nonclassical ionic structures or electronically delocalized radicals etc. It is then possible to use this criterion to obtain information regarding the nature of the radicals or ions formed. (compare *e.g.* section III).

A. Effects of α -Substitution. – a) *Replacing -H with -alkyl groups in H_3C-X bonds.* In Table 4 the effects on the bond dissociation energies upon substituting alkyl groups for hydrogen in H_3C-X bonds are summarized as differences between the $DH_{298}^0(CH_3-X)$ and the $DH_{298}^0(CR_3-X)$ values. The differences ΔDH^0 for the homopolar bond breaking are listed as top entries (fatter print), those for the heteropolar ΔD^*H^0 as bottom entries in Table 4.

Table 4. Differences in H_3C-X Bond Dissociation Energies replacing H with alkyl groups, expressed as $[D^*H^0(H_3C-X) - D^*H^0(R_3C-X)] = \Delta D^*H^0$ and $[DH^0(H_3C-X) - DH^0(R_3C-X)] = \Delta DH^0$
Effects of α -Substitution on the Strength of C-X Bonds

R_3C-X	-H	-CH ₃	-F	-Cl	-Br	-I	-OH	-OCH ₃	-NH ₂	-NO ₂
CH ₃ , H, H ^a)	6 39	3 37	2 36	3 36	2 35	3 36	0 32	0 <33	2 35	2 34
C ₂ H ₅ , H, H ^a)	6 45	3 42	2 42	4 42	2 41	3 41	0 39	0 <38	2 41	1 40
CH ₃ , CH ₃ , H ^a)	9 62	4 57	3 56	3 57	3 55	3 56	0 52	0 53	2 55	1 53
CH ₃ , CH ₃ , CH ₃ ^a)	12 79	6 73	0 67	3 70	4 70	6 72	0 66	0 <67	3 70	2 68

^a) Substituents R in R_3C-X

These data lead to the following conclusions:

a) With the exception of R_3-OH and R_3-OCH_3 , replacing -H with alkyl groups lowers the energies required to break C-X bonds *hetero-* or *homolytically*. The observed

differences in bond dissociation energies with increasing alkyl-substitution are much larger, both on an absolute and a percentage basis for hetero – than homopolar bond breakage.

b) Comparing the first two sets of entries it becomes evident, that the β -substituent effect in the case of DH^0 is indeed negligible. For the heteropolar D^*H^0 a stabilizing effect of 6 kcal mol⁻¹ can be derived.

c) For R_3C-X bonds where $X = H$ or alkyl, the relative substituent effects observed for homo- and heteropolar bond dissociation energies parallel each other, contrary to more polar R_3C-X bonds.

d) Denoting the overall effect of replacing all three hydrogen atoms in CH_3-X by methyl groups 'total', the replacement of the first hydrogen atom always lowers the heteropolar D^*H^0 by about 50% of the 'total' effect and each additional methyl group by about 25%. The same behaviour is observed for homopolar bond breaking, involving the non-polar R_3C-H and R_3C-CH_3 bonds. For more polar bonds such as R_3C-F , R_3C-OH and R_3C-OCH_3 the α -alkyl substituent effect is reduced and effectively non existent for the two latter bonds.

The effect of alkyl substituents on the energy required for breaking R_3C-X bonds *heterolytically* into the corresponding carbonium ions R_3C^+ and X^- anions as shown in Table 4 are readily rationalized on the basis of stabilizing effects of the alkyl groups. *Brauman et al.* [10] have suggested a polarizability stabilization by alkyl groups, which is a reasonable concept in view of the fact that α -alkyl groups also stabilize negative charges.

Considering the complete charge separation attained in the heteropolar bond breaking process it is to be expected that any polarization of alkyl groups by the induced dipoles in the ground state bond is swamped out by the much larger stabilization of the carbonium ion center evolving in the transition state. It is then not surprising, that the magnitudes of the substituent effects are about the same, irrespective of the nature of X^- . It is interesting to note however, that for $X = -OH$, $-OCH_3$, $-NO_2$ and $-F$, the substituent effects are at a relative minimum (about 5 to 10 kcal mol⁻¹ lower) compared to $-CH_3$ and $-H$, which is perfectly in line with expectation based on the differences in polar character of the respective bonds.

The data for R_3C-OCH_3 constitute upper limits, the true values must be expected to be *lower* than those for R_3C-OH , to agree with the data on relative gas phase acidities of alcohols observed in the ion-cyclotron resonance studies [9]. It is evident however, that the polarizability stabilization of alkyl groups on anionic centers is much smaller than on cationic centers.

The effect of α -alkyl substituents on the energy required for *homopolar* bond breaking can similarly be interpreted in a consistent manner in terms of the polarizability of alkyl groups by induced partial charges. To the extent that the bonds already comprise partial charge separation in the ground state, less of a change in charge density and consequently less of a change in polarization of the alkyl groups bonded to the carbon centers evolving as radicals, is observed.

b) *Replacing -H with -halogens in H_3C-X bonds.* The lack and the uncertainties of thermodynamic data on mixed haloalkanes renders any conclusions concerning the effects of α -halogen atoms on the strength of adjacent R_3C-X bonds tentative.

From the data given in reference [1] some trends become apparent however, which are considered to be outside the experimental error limits.

In Table 5 the differences in bond dissociation energies, expressed as $DH^\circ(\text{H}_3\text{C}-\text{X}) - DH^\circ(\text{R}_3\text{C}-\text{X})$ and $D^*H^\circ(\text{H}_3\text{C}-\text{X}) - D^*H^\circ(\text{R}_3\text{C}-\text{X})$ are listed.

Table 5. Differences in $\text{H}_3\text{C}-\text{X}$ Bond Dissociation Energies replacing H with halogens, expressed as $[DH^\circ(\text{H}_3\text{C}-\text{X}) - DH^\circ(\text{R}_3\text{C}-\text{X})]$ and $[D^*H^\circ(\text{H}_3\text{C}-\text{X}) - D^*H^\circ(\text{R}_3\text{C}-\text{X})]$ respectively.
Effects of α -Substitution on the Strength of C-X Bonds

$\text{R}_3\text{C}-\text{X}$	-H	-CH ₃	-F	-Cl	-Br	I
F, H, H ^a)	2 12	-3 (15)	-13 -63	(-5) -50	(-3) -43	
F, F, H ^a)	1 27	-8 (19)	-19 -55	-4 -34	(0) -26	
F, F, F ^a)	-2 (11)	-11 (1)	-21 (-8)	-2 (11)	1 (13)	3 (15)
Cl, H, H, ^a)	3 (13)	-1 (9)	(-4) (6)	3 (13)	(5) (15)	
Cl, Cl, H ^a)	5 (50)	-1 (45)	(0) (45)	6 (51)	(10) (55)	4 (49)
Cl, Cl, Cl ^a)	8 39	1 (32)	5 36	11 42	15 46	
Br, H, H ^a)	3 (13)	-1 (8)	(-2) (8)	(5) (15)	(6) (16)	
Br, Br, H ^a)	(1) (50)	(-5) (46)	(-4) (47)	(6) (56)	(8) (58)	
Br, Br, Br ^a)	8 (53)	(-10) (53)	(-6) (39)	(5) (50)	14 (59)	
I, H, H ^a)	2 (24)	-2 (21)				5 (27)

^a) Substituents R in $\text{R}_3\text{C}-\text{X}$.

Positive numbers then indicate a reduction, negative members an increase in the bond dissociation energy upon halogen substitution. Data in parentheses refer to unreliable homopolar bond dissociation energies, based on estimated heats of formation of the molecule. Discrepancies based on those data should not be given too much weight. With few exceptions all heteropolar values have relatively large error limits attached to them, and conclusions drawn from those data must be viewed with caution. The top entries refer again to differences in homopolar bond dissociation energies, bottom entries to differences in heteropolar bond dissociation energies.

It is reasonable to consider chloro-, bromo- and iodo alkanes separately from fluoroalkanes.

For Cl-, Br- and I-alkanes the data listed in Table 5 allow the following conclusions:

Halogen atoms (Cl, Br, I) α to a C-H bond generally reduce both the homopolar DH° and the heteropolar D^*H° . The effect on the homopolar $DH^\circ(\text{C}-\text{H})$ appears to be additive, and largely independent of the nature of the halogen atoms, and is about $2.5 \text{ kcal mol}^{-1}$ per α -halogen substituent.

Halogen atoms (Cl, Br, I) α to a C-CH₃ bond have apparently little effect if any on $DH^\circ(\text{C-CH}_3)$.

Halogen atoms (Cl, Br, I) α to C-X bonds (where X = Cl, Br, I) appear to have a similar effect on $DH^\circ(\text{C-X})$ as is observed for C-H bonds, *i.e.* an additive reducing effect on $DH^\circ(\text{C-X})$ largely independent on the nature of the halogen substituent. The effect can be estimated at between 3 and 5 kcal mol⁻¹.

For *alkyl fluorides* the data listed in Table 5 cannot readily be interpreted in terms of an apparent α -fluorine substituent effect.

Some trends appear to be real however:

Fluorine substituents α to C-H bonds appear to have no or little effect on the homopolar or the heteropolar C-H bond dissociation energy.

Fluorine substituents α to C-CH₃ bonds on the other hand increase the homopolar bond strength by about 3 to 5 kcal mol⁻¹ per fluorine atom.

C-F bond strengths, $DH^\circ(\text{C-F})$, appear to be drastically increased by α -fluorine substituents in contrast to only a small effect if any onto $DH^\circ(\text{C-X})$, where X = Cl, Br, I.

Homopolar C-F bond strengths appear to be only slightly affected by adjacent α -halogen (Cl, Br, I) substituents.

Considering the large uncertainties attached to *heteropolar* bond dissociation energies, only tentative conclusions can be drawn from these data. Some interesting aspects are noteworthy however. Firstly, except for fluorine, replacement of α -hydrogens by halogen atoms generally lowers the $D^*H^\circ(\text{C-X})$ by more than 10 kcal mol⁻¹. The second halogen substituent appears to exercise an even larger stabilizing effect on the R₃C⁺ ion than the first one, while the introduction of the third halogen atom seems to have little or even a destabilizing effect.

The general effect of fluorine substituents α to C-H and C-CH₃ bonds appears to be essentially similar to those observed for Cl, Br and I, *i.e.* a lowering of the corresponding D^*H° . As was observed for Cl₃C-X and Br₃C-X bonds, the data for the triply halogenated F₃C-H and F₃C-CH₃ bonds do not follow the trend towards lower values for D^*H° with increasing α -substitution observed for H₃C-X > H₂halC-X > H(hal)₂C-X. The deviation appears to be too large to make this purely an error limit artifact. The apparent outstanding behaviour, *i.e.* relative instability of [C(hal)₃]⁺ ions would of course have to be related to the high symmetry of these planar ions and the absence of different C-X bonds in the molecule.

The effect of α -fluorine substituents adjacent to R₃C-X bonds where X = Cl, Br, I are obviously quite different from chlorine, bromine or iodine substituents. The replacement of one hydrogen atom in CH₃-Cl with fluorine drastically increases $D^*H^\circ(\text{G-Cl})$ while the introduction of the second and third fluorine in CHF₂-Cl work in the opposite direction. This behaviour is observed for C-F, C-Cl and C-Br bonds and thus appears to be real. It is then evident, that at least two effects are operative, one stabilizing, one destabilizing R₃C⁺ cations, where R = F or H.

Another general trend is noteworthy: α -halogen substituents (Cl, Br, I) have about the same lowering effect on $D^*H^\circ(\text{R}_3\text{C-X})$ irrespective of the bond broken, with a tendency towards slightly smaller effects with C-CH₃ and C-F bonds. The same effect

has been observed for α -alkyl substituents and was discussed in terms of polarizability stabilizations. The observed α -substituent effects of halogens on the heteropolar strengths of the adjacent bonds can be rationalized with the simple concepts of 'resonance', 'polarizability', 'inductive' effects and combinations thereof.

B. 'Extra' Stabilization from Electronic Delocalization. – It is a well known fact that the formation of a radical or ionic center adjacent to a π -bond may be accompanied by a 'resonance' or stabilizing effect, *i.e.* a delocalization of electrons resulting in thermodynamically more stable structures.

'Extra' stabilization energies (E_s) for radicals and ions are defined as the differences in dissociation energies of a given bond β to a π -bond ($R_\pi A-X$ e.g. $C=C-A-X$) compared to the corresponding bond in the parent saturated molecule ($RA-X$ e.g. $C-C-A-X$).

$$E_s(R_\pi A^\cdot) = DH_{298}^\circ(RA-X) - DH_{298}^\circ(R_\pi A-X)$$

and

$$E_s(R_\pi A^+) = D^*H_{298}^\circ(RA-X) - D^*H_{298}^\circ(R_\pi A-X)$$

The data for the DH° and D^*H° can be taken from ref. [1]. For the allyl-radicals e.g., the calculation (in kcal mol⁻¹) would give







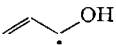

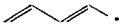







$$\begin{aligned} E_s(\text{allyl}^\cdot) &= DH_{298}^\circ(\text{CH}_3\text{CH}_2\text{CH}_2\text{-H}) - DH_{298}^\circ(\text{CH}_2\text{CHCH}_2\text{-H}) \\ &= 98 - 88.6 = 9.4 \end{aligned}$$

Experimental data on stabilization energies of radicals is sparse and the few values reported show very large discrepancies. The complexities of the reaction systems studied and the uncertainties inherent in the kinetic methods used (particularly the toluene carrier technique), as well as the assumptions applied, resulted in experimental data for the allyl radical ranging from 10 to 25 kcal mol⁻¹. Even though the values for the extra stabilization energies of some of the more classic delocalized radicals such as allyl and benzyl have now been experimentally fixed using various techniques, the data for most other radicals— and particularly for the ions still have considerable uncertainties attached to them.

The available 'best' experimental data are listed in *Table 6* together with estimated confidence limits, based on the observed experimental error limits and the uncertainties inherent in the method.

Most of the reliable data have been obtained using either the iodine atom abstraction or the small ring compound pyrolysis method. As was mentioned previously [1], the largest uncertainty in the iodine method arises from the assumption, that the activation energy (E_x) for the reverse reaction, $HI + R^\cdot \xrightarrow{x} RH + I$ be 1 ± 1 kcal mol⁻¹. While this assumption has been shown to be valid for saturated C-H bonds and for 'allylic' bonds in mono-olefins, it appears to be seriously in error in the case of the pentadienyl-H bond. To provide agreement between the values obtained using the iodine method and the small ring compound pyrolysis method, E_x for the pentadienyl radical would have to be about 5 kcal mol⁻¹ which may not be unreasonable in view of the thermoneutrality of this reaction. In this context it is interesting to

Table 6. 'Extra' Stabilization Energies (E_s) in Delocalized Radicals^{a)} and Ions

Radical ^{b)} or Ion	$E_s^1)$	Ref.
	9.6 ± 1.5	[11] [12]
	(12)	[13] [3]
	12.6 ± 1.5	[14]
	(13)	[3]
	13.1 ± 1.5 (7.8 ± 1.5) ^{e)}	[15] [16]
	9.4 ± 2	i)
	11.4 ± 2.2 (10.8 ± 2.5)	[17] h)
	12.6 ± 1.5	[18]
	$20 \pm 2^c)$	[19] [20]
	15–20	[21]
	24.6 ± 2.5	[22]
	21 ± 2	[23]
	(49)	[23]
	23.4 ± 2.5	[24]
	12.5 ± 1.5	[25]
	(21) ^{g)}	[3]

Radical ^{b)} or Ion	E _s ¹⁾	Ref.
	4-9	[26] [27]
	(~3)	[8]
	24 ^{f)}	[28]
	(O) ^{d)}	[29] [30]
	(2.7) ^{d)} (7)	[31] ^{d)}
	14.5 ± 2	[32]
	~7 ± 3	^{k)}

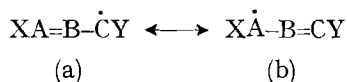
^{a)} E_s is defined as the difference in bond energies between the parent saturated bond and the 'allylic'-type bond and represents the 'extra' stabilization energy, which does not include the π-conjugation energy in the ground state molecule, ^{b)} For convenience of presentation the radicals are depicted in the localized form, ^{c)} mean value from reference 19 and 20, ^{d)} Value in dispute. Contrary to the value quoted (obtained from halogen atom technique) biradical analyses of ring compound pyrolyses indicate values of ~7 kcal mol⁻¹ for E_s. (compare A. T. Cocks & K. W. Egger, J. chem. Soc. Perkin II, 1973, 197 and 199, ^{e)} This lower value is probably due to the stabilization of alkyl radicals by α-halogen atoms rather than to a lower stabilization energy of the unsaturated system. Compare text, ^{f)} Independent of reactant (allene, propyne, butadiene) the structure of the ion was reported as that of the propargylon

[28], ^{g)} The isomerization step C₆H₅CH₂⁺ → cyclo-C₇H₇⁺ is in all probability exothermic by about 7 kcal mol⁻¹ and the stabilization energy of the intermediate benzylation would then be masked by the much higher delocalization energy gained in cyclo-C₇H₇⁺. On the basis of C₆H₅CH₃ → cyclo-C₇H₇⁺ + H⁻, taking the change from a 'primary' exo to a 'secondary' ring carbon atom into account, a value of 32 kcal for E_s cyclo-C₇H₇⁺ (via C₆H₅CH₂⁺) is calculated compared to 49 for the direct formation cyclo-C₇H₈-cyclo-C₇H₇⁺ + H⁻, ^{h)} Based on DH^o(CH₂CHCH(OH)-H) = 81.6 and an estimated value for DH^o(CH₃CH₂CH(OH)-H) of 92.4 arrived at from the consistencies of DH^o for CH₃-H (104), C₂H₅-H (98), *i*-C₃H₇-H (92), H₂C(OH)-H (95.6) and (CH₃)₂C(OH)-H (90.3) [34], ⁱ⁾ Based on the experimental value of 88.6 kcal mol⁻¹ for DH^o(CH₂CHCH(Cl)-H) compared to 98 kcal for DH^o(CH₃CH₂-H) taking into account that in general halogens appear to have small if any inductive stabilizing effects when bonded to a carbon radical (DH^o(CH₃-H) = 104 and DH^o(CH₂Cl-H) = 103 (compare text), ^{k)} Unpublished data obtained from the pyrolysis of

A. T. Cocks), ¹⁾ Error limits refer to confidence limits estimated by the authors. Where no limits are given, the data are subject to larger uncertainties.

note that the similar reaction $\text{HNO} + \text{C}_6\text{H}_6 \longrightarrow \text{C}_6\text{H}_5 + \text{NO}$ requires $9.2 \text{ kcal mol}^{-1}$ activation energy [22].

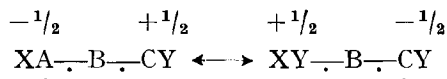
A similar discrepancy between the data obtained using the iodine atom (and bromine atom) method and the results from small ring pyrolysis studies is observed for radicals of the type $\text{O}=\text{C}-\dot{\text{C}}$. The theoretical interpretation of such 'stabilizing' effects – particularly for 'aromatic' structures (fulfilling the Hueckel $4n + 2$ rule) such as $\text{cyclo-C}_5\text{H}_5^-$, $\text{cyclo-C}_7\text{H}_7^+$ etc. has attracted considerable interest. A variety of molecular orbital and valence bond approximations have been presented. In terms of a resonance hybrid valence bond formulation at least two hypothetical structures – schematically represented below as (a) and (b) – can be visualized for 'delocalized' radicals:



Depending on the nature of A, B and C and the substituents X and Y the two structures may have considerably different thermodynamic stabilities.

It has been suggested [29]–[31], that large stabilization energies are only to be expected for those radicals, which allow for equal or closely equal thermodynamic stabilities of the two canonical structures (a) and (b). This would essentially be the case, whenever A and C are equal, as is the case *e.g.* with $\text{C}=\text{C}-\dot{\text{C}}$ and $\text{C}=\text{N}-\dot{\text{C}}$, but not for $\text{O}=\text{C}-\dot{\text{C}}$, $\text{C}=\text{C}-\dot{\text{N}}$ or $\text{C}\equiv\text{C}-\dot{\text{C}}$ type radicals. Differences in the heats of formation of the two hypothetical structures (a) and (b) would then be directly reflected in a lowering of the stabilization energies. Any relationship between the lowering of E_s and the expected differences in thermodynamic stabilities of the structures (a) and (b) cannot be determined as some of the pertinent data such as that for the acetylonyl-type radicals are still in dispute.

It has been suggested that the stabilization energies can be considered a composite of a dominant delocalization energy term originating from delocalization of the unpaired electron between centers A, B and C, reducing electron-electron repulsion and a possible electronic interaction energy term. Using schematic valence-bond structures [33], this has been represented with 3-electron bond structures and a semi-ion pair type charge separation.

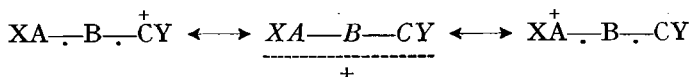


One might then expect an 'inductive' stabilizing effect of the substituents X and Y.

The stabilization energies listed in table 6 appear to substantiate the concept of such an additional small inductive effect for *alkyl* substituents whereby the substitution of the first hydrogen atom by an alkyl group would have a much more pronounced effect compared to the introduction of further alkyl substituents. To what extent the observed differences in E_s of about 2.5 to 3 kcal between the allyl- and methallyl radicals indeed reflect a real substituent effect remains doubtful however, particularly in view of the fact, that the introduction of a second methyl group in α - or β -position has no apparent effect at all. On the other hand OH and Cl (compare

footnote h table 6) bonded to the radical center seem to have little or no effect which would be in accord with the lack of an appreciable substituent effect of OH or Cl in the case of saturated radicals and ions, as was discussed previously in this section.

Considering the uncertainties in the data for $\Delta H_f^\ddagger(R^+)$ the values derived for the stabilization energies generated in the corresponding 'delocalized' carbonium ions listed in table 6 are to be viewed with caution. Nevertheless the data imply, that allyl- and methallyl carbonium ions when compared with the corresponding saturated alkyl species essentially involve the same amount of stabilization energies as the corresponding radicals and vice versa. The concept of a reduction of electron repulsion due to delocalization of the π -electrons provides a simple and reasonable rationale for the consistency between radicals and ions.



In contrast, a large increase in 'delocalization' energy is observed between the cycloheptatrienyl radical and the cycloheptatrienyl cation. This is a consequence of the particularly stable 'aromatic' structure of cyclo-C₇H₇⁺, satisfying the Hückel 4n + 2 rule.

HMO calculations are in general accord with these experimental findings, predicting about equal amounts of delocalization energies for the allyl radical and -ion but much larger delocalization in cyclo-C₇H₇⁺ compared to cyclo-C₇H₇.

The high value for E_s(C₆H₅⁺CH₂) compared with C₆H₅CH₂ again is not surprising in view of the well-known isomerization of benzylcations into the 'aromatic' tropylium cation [13] [34].

The relatively large difference in 'extra stabilization' of 15 kcal or more observed for the C₃H₃⁺ compared to the C₃H₃· radical is noteworthy and would imply different hypothetical structures for the radical and ion. For the ion a propargyl structure has been proposed.

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151. Spectre de Résonance Paramagnétique Electronique de la Diphénylthiophosphine cristalline irradiée aux rayons X

par Michel Geoffroy

Département de Chimie physique, Ecole de Chimie, Université de Genève
 30, quai de l'Ecole de Médecine, 1211 Genève 4 – Suisse

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Summary. The electron spin resonance spectra of X-irradiated diphenylphosphine sulfide monocrystal and powder are reported. The results show that the radical $\Phi_2\dot{P}S$ is mainly produced. The values and directions of the principal components of \bar{g} and ^{31}P -hyperfine tensors are determined.

Introduction. – L'irradiation aux rayons X d'une substance cristalline contenant une liaison P–H permet fréquemment de piéger une espèce radicalaire pour laquelle l'électron non apparié est fortement localisé sur l'atome de phosphore [1–2]. L'étude par Résonance Paramagnétique Electronique (RPE.) de tels monocristaux et poudres irradiés permet alors d'obtenir directement des renseignements sur la configuration électronique du phosphore et d'avoir ainsi de l'information sur l'éventuelle participation des orbitales d de cet atome.

Nous reportons dans ce mémoire les résultats concernant le radical $(C_6H_5)_2\dot{P}=S$ piégé dans des cristaux de diphénylthiophosphine irradiés.

Partie expérimentale – La diphénylthiophosphine a été synthétisée à partir de la diphénylphosphine (produit *Alfa*) d'après la méthode de *Peters* [3]. Des monocristaux de grandes dimensions ont été obtenus par lente évaporation d'une solution dans l'acétonitrile. L'irradiation aux rayons