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The Dehalogenation Reaction of Organic Halides by Tributyltin Radical: The Energy of Activation vs. the BDE of the C-X Bond

Carlo Galli* and Tullia Pau

Dipartimento di Chimica and Centro CNR Meccanismi di Reazione,
Università 'La Sapienza', 00185 Roma, Italy

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***Abstract*:** The energy of activation (E_a) of the dehalogenation reaction induced by $Bu_3Sn^•$ was measured for some aryl, alkyl and benzyl halides. BDE values of the C-X bond undergoing homolysis were obtained from thermochemical cycles, and correlated with the E_a values. No major effect due to the polarity of the C-X bond was found. Durene derivatives showed a buttressing effect. A comparison of the homolytic BDE of the C-X bond of organic halides with the BDE of the C-X bond in the radical anion of the same precursors is reported.

Dehalogenation of alkyl, aryl, or vinyl halides (RX) by means of trialkyltin radicals (eq. 1) is an important synthetic procedure: it provides an easy access to the corresponding radical species ($R^•$), enabling further structural modifications.[1]

$$Bu_3SnH \xrightarrow{AIBN} Bu_3Sn^• \xrightarrow{RX} Bu_3SnX + R^• \qquad (1)$$

However, little information is available concerning the reactivity of the substrate in this process. While this information would be valuable for a proper planning of synthetic conditions, it is also useful for a deeper understanding of the fundamental features of radical processes.

In a seminal investigation,[2] Curran and co-workers determined the rate constants for the reaction of $Bu_3Sn^•$ with a number of aryl and vinyl halides. We have extended this study to include a wide variety of substrates. The energy of activation (E_a) of the halogen-abstraction step of eq. 1 has been determined for representative substrates. A correlation of these E_a values with the corresponding bond dissociation energy (BDE, i.e., D(R-X)) values of the C-X bond undergoing homolysis has been sought by the use of the Evans-Polanyi relationship (eq. 2),[3] in order to provide an indication of the extent of halogen transfer in the transition state of the process.

$$E_a = \alpha\ D(\text{R-X}) + \text{cost} \qquad (2)$$

The values of D(R-X) required to establish the correlation have been obtained from Δ_fH_{298} values and thermochemical cycles. An outline of this investigation follows. The homolytic BDE of the C-X bond of two organic halides and the corresponding BDE in the radical anion of the same compounds are compared.

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Results

Determination of the rate constants of the dehalogenation process. Relative reactivities were obtained from competition experiments of a given substrate (R-X) with a reference substrate (R'-X) toward a defect of tin radical at 80 °C in benzene solution (eq. 3). The multistep reaction mechanism is delineated in Scheme 1.[2]

$$\text{R-X / R'-X} \xrightarrow{\text{Bu}_3\text{SnH/AIBN}} \text{R-H / R'-H} \quad (+\ \text{Bu}_3\text{SnX}) \qquad (3)$$

$$\text{R-X} + \text{Bu}_3\text{Sn}^\bullet \xrightarrow{k_{RX}} \text{R}^\bullet + \text{Bu}_3\text{SnX}$$
$$\text{R}^\bullet + \text{Bu}_3\text{SnH} \rightarrow \text{R-H} + \text{Bu}_3\text{Sn}^\bullet$$

$$\text{R'-X} + \text{Bu}_3\text{Sn}^\bullet \xrightarrow{k_{R'X}} \text{R'}^\bullet + \text{Bu}_3\text{SnX}$$
$$\text{R'}^\bullet + \text{Bu}_3\text{SnH} \rightarrow \text{R'-H} + \text{Bu}_3\text{Sn}^\bullet$$

Scheme 1

Quantification of the relative amounts of products R-H and R'-H allowed the determination of the relative reactivity of the two substrate (k_{rel}) in the dehalogenation step. Depending on convenience, one out of two standard substrates, whose rate of dehalogenation by $\text{Bu}_3\text{Sn}^\bullet$ at 80 °C was known, was used as the relay compound. These substrates were 2-bromobenzonitrile ($k_{R'X} = 1.6 \times 10^7\ M^{-1}\ s^{-1}$) and 3-bromoanisole ($k_{R'X} = 4.0 \times 10^6\ M^{-1}\ s^{-1}$).[2] In this way, the relative reactivities could be converted into absolute rates for halogen abstraction from all the substrates investigated, chosen among most basic examples of organic halides. The rate constants for dehalogenation at 80 °C are reported in Table 1, which also includes relevant values from the previous investigation.[2]

Inspection of the reactivity data of Table 1 shows that, holding the R group of the precursor constant, iodides are more reactive than bromides, which in turn are more reactive than chlorides. Within the same halide series, the benzoyl and alkyl derivatives are more reactive than the aryl and vinyl compounds. Aromatic positional isomers do not differ significantly in reactivity, and the effect of substituents is not pronounced. All these experimental findings appear to be bound to the different strength of the C-X bonds undergoing homolysis: the stronger the bond, the slower the halogen abstraction process. They also confirm the view[1] that the dehalogenation of the substrate by $\text{Bu}_3\text{Sn}^\bullet$ represents the rate determining step of the process (Scheme 1).

Finally, it was verified that use of either one of the two relay compounds, in competition with a specific substrate, affords values of the dehalogenation rate that are the same within experimental errors. This check, assuring that the reactivity of substrate given in Table 1 is independent on the relay compound employed, indicates that the incursion of halogen exchange processes (as in eq. 4) during the competition experiments is negligible.

$$\text{R}^\bullet + \text{R'-X} \rightarrow \text{R'}^\bullet + \text{R-X} \qquad (4)$$

A correlation between the energy of the bond undergoing homolytic cleavage and the reactivity in the dehalogenation reaction is provided within the framework of the extrathermodynamic Evans-Polanyi relationship (eq. 2).[3] The energy of the bond being cleaved is expressed by the BDE term. For consistency, the reactivity of the process must also be expressed by an enthalpic parameter, such as the Arrhenius activation energy. The higher the value of the correlation parameter α, the more advanced will be the bond cleavage in species,[4] more reliable D_{298}(Ph-X) data have been obtained for PhCl, PhBr, PhI as 97.6, 82.6, and 67.2 kcal/mol, respectively (Table 2). In a similar way, from a very recent determination of $\Delta_f H_{298}(\mathrm{PhCH_2}\cdot)$ as 49.7 kcal/mol,[6] we obtain a series of updated values of D_{298}(R-X) for the benzyl halides (Table 2).

Studies of pyrolysis in the gas phase indicate the α C-H bond of naphthalene as 1.9 kcal/mol *weaker* than that of benzene,[7] and the β C-H bond as 0.3 kcal/mol weaker.[7] Since the D_{298}(C-H) of benzene is 113.45 kcal/mol,[5] the α and β D_{298}(C-H) of naphthalene result to be 111.6 and 113.2 kcal/mol, respectively. From these data, and from the known values of $\Delta_f H_{298}(\mathrm{H}\cdot)$ (52.1 kcal/mol) and of $\Delta_f H_{298}$(naphthalene) (35.99 kcal/mol),[4] eq. 5 provides the $\Delta_f H_{298}$(α-naphthyl•) and $\Delta_f H_{298}$(β-naphthyl•) values as 95.4 and 97.0 kcal/mol, respectively. Finally, from the latter values and from the enthalpies of formation of the α- and β-halonaphthalenes,[4c] the corresponding D_{298}(Ar-X) values (Table 2) are obtained. Unfortunately, the $\Delta_f H_{298}$(α-*bromo*naphthalene) is not experimentally available. However, since it is reported that the BDE of α-bromonaphthalene is 0.5 kcal/mol *lower* than that of β-bromonaphthalene,[7,8] the BDE of the former can be obtained (i.e., 81.2 kcal/mol); thus, the missing value of $\Delta_f H_{298}$(α-bromonaphthalene) can be calculated to be equal to 40.9 kcal/mol.

Table 2. Available thermochemical data (in *italics*)[a] and new ones obtained in this study

R [$\Delta_f H_{298}(\mathrm{R}\cdot)$]	$\Delta_f H_{298}$(RH)	D_{298}(R-H)	$\Delta_f H_{298}$(RX)	D_{298}(R-X)
phenyl *[81.1]*	*19.75*	*113.45*	PhCl *12.4*	97.6
			PhBr *25.2*	82.6
			PhI *39.4*	67.2
benzyl [*49.7*]	*11.97*	*89.8*	$\mathrm{PhCH_2Cl}$ *4.47*	74.1
			$\mathrm{PhCH_2Br}$ *15.2*	61.2
			$\mathrm{PhCH_2I}$ *23.9*	51.3
1-naphthyl [95.4]	*35.99*	111.6	1-Cl-naph. *28.6*	95.7
			1-Br-naph. 40.9[b]	81.2
			1-I-naph. *55.9*	65.0
2-naphthyl [97.0]	*35.99*	113.2	2-Cl-naph. *32.8*	93.1
			2-Br-naph. *42.0*	81.7
			2-I-naph. *56.2*	66.3
9-anthracenyl [112.5]	*55.04*	109.6	9-Br-anthr. 62.1[b]	77.1
ethenyl [*71.7*]	*12.55*	*111.2*	Cl-ethene *9.10*	91.5
			Br-ethene *18.93*	79.5
$\mathrm{Me_3Sn}$ [31.6]	-	-	$\mathrm{Me_3SnCl}$ -	107 (extr)[b]
			$\mathrm{Me_3SnBr}$ *-33.0*	91.3
			$\mathrm{Me_3SnI}$ *-19.7*	76.8

[a] Literature data are from refs. 4-9, and are in kcal/mol [b] Obtained from extrapolation, see text.

For position 9 of anthracene D_{298}(C-H) is reported to be 3.9 kcal/mol *lower* than the D_{298}(C-H) value of benzene;[7] therefore a value of 109.6 kcal/mol is obtained for the BDE of that bond. From this value, the Δ_fH_{298} value for 9-anthryl· radical results to be equal to 112.5 kcal/mol, using the known Δ_fH_{298}(anthracene) (i.e., 55.0 kcal/mol) and Δ_fH_{298}(H·) values.[4] The Δ_fH_{298}(9-bromoanthracene) is not experimentally available; however, the C-Br bond of 9-bromoanthracene is reported as 5.5 kcal/mol *weaker* than that of PhBr from pyrolysis studies.[8] This datum gives a value of 77.1 kcal/mol for the D_{298}(C-Br) of 9-bromoanthracene, and allows one to reckon the enthalpy of formation of 9-bromoanthracene as 62.1 kcal/mol.

A D_{298}(C-H) of 111.2 kcal/mol has been determined for ethylene,[9] as well as a Δ_fH_{298}(CH_2=CH·) of 71.7 kcal/mol.[9] Thus, knowledge of the Δ_fH_{298} (chloroethene) (9.10 kcal/mol) and Δ_fH_{298} (bromoethene) (18.93 kcal/mol),[4c] gives the corresponding D_{298}(C-X) values (Table 2). It can be assessed that the errors associated with the present evaluations of D_{298}(R-X) are within ± 0.2 - 0.4 kcal/mol.

Energy of activation of the dehalogenation reaction. The energy of activation E_a for the dehalogenation induced by $Bu_3Sn^\bullet$ has been determined experimentally for those organic halides whose D_{298}(C-X) is available (see previous section). Competition experiments have been run between a given substrate and a reference substrate with a deficiency of $Bu_3Sn^\bullet$ (see Scheme 1) in toluene solution at three temperatures in the 70 - 110 °C interval. In general, the relay substrate was 3-bromoanisole,[2] whose E_a for the reaction with $Bu_3Sn^\bullet$ is calculated to be 7.0 kcal/mol (ln A being 25.3 M^{-1} s^{-1}). Each k_{rel} value obtained at a given temperature was multiplied by the rate constant of the relay substrate, in order to obtain the absolute rate constant of the competing substrate (Table 3). The Arrhenius plot of the rate constants provided the E_a and ln A parameters for the various substrates examined. In the course of the investigation, as new values of E_a and ln A became available for substrates other than 3-bromoanisole, these ones were employed in turn as relay compounds. This procedure aided the GC analytical separation. Due to the use of toluene as the solvent, simple benzylic precursors could not be directly investigated; their reactivity in this reaction was evaluated by investigating the corresponding *p*-methylbenzylhalides (i.e., *p*-xylene was the reduced product). Unfortunately, polymerization of β-bromostyrene became prevalent over hydrodebromination on raising the reaction temperature, thus preventing the determination of the activation parameters for this particular substrate. The values of the present determinations of E_a are affected by an error of ± 0.4 - 0.8 kcal/mol.

Discussion

Correlation of E_a vs. D(C-X). In keeping with the Evans-Polanyi relationship (eq. 2),[3] the E_a data of the $Bu_3Sn^\bullet$ induced dehalogenation reaction of the *bromoderivatives* (Table 3) are correlated with the corresponding *D*(C-X) data (Results section).[10] A rather good straight line is obtained, with a slope (α) equal to 0.12 (Fig 1). This indicates an *early* TS for the reaction. The correlation embraces 3-bromoanisole, which was tentatively assigned the *D*(C-Br) value of PhBr, α-bromonaphthalene, 9-bromoanthracene, α-bromo-*p*-xylene,[11] and 1-bromohexadecane as an example of a primary alkyl bromide.[12] The response of these bromoderivatives fulfils the expectation that the reaction with $Bu_3Sn^\bullet$ becomes faster as the C-X bond becomes weaker. The structure of the precursors can vary considerably without any major prejudice to the correlation, which may be assigned to the same degree of bromine atom transfer taking place in the TS. In the correlation of Fig 1, 3-bromodurene (durene is 1,2,4,5-tetramethylbenzene) is decidedly off the line. The presence of the two β methyl groups in *ortho* position with respect to the two α methyl groups flanking the halogen atom, has the effect of compressing the two α methyl groups and appears to *enhance* the ease of abstraction of bromine, as if the $BDE_{C\text{-}Br}$ were *decreased* in value in this compound (ca. 7%, by extrapolation) with respect to the model compound PhBr. This result may be viewed as an example of a favourable buttressing effect,[13] and represents a novel finding in radical processes.

The iodo- and chloroderivatives lend themselves to analogous E_a *vs.* *D*(C-X) correlations (Fig 2 and 3). It can be noticed that the extent of the above mentioned buttressing effect varies as the size of the halogen in 3-halodurene is changed. With the larger bromo and iodo substituents, the reactivity of 3-halodurene falls outside the correlation, whereas the smaller size of the substituent in 3-chlorodurene does not cause any odd reactivity. By extrapolation of the correlation of Fig 3, it can be evaluated that the BDE of I-DUR is ca. 30% lower than that of PhI. The α value of the Evans-Polanyi type relationships, namely, the slope of the three correlations (Figs 1-3), does not appear to vary appreciably from the chloride to the iodide series. A direct comparison of the three series would be allowed by presenting them in one plot.

Fig 1

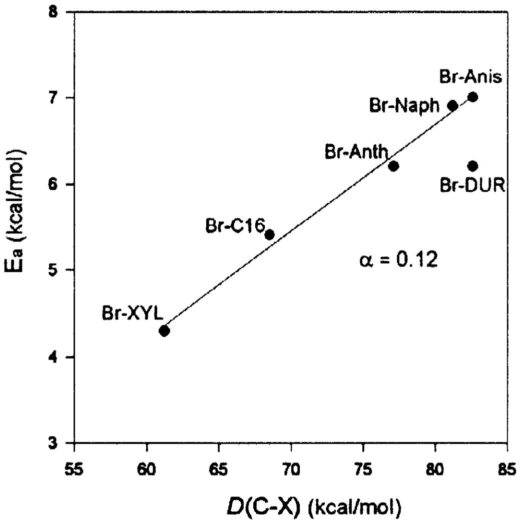


Fig 2

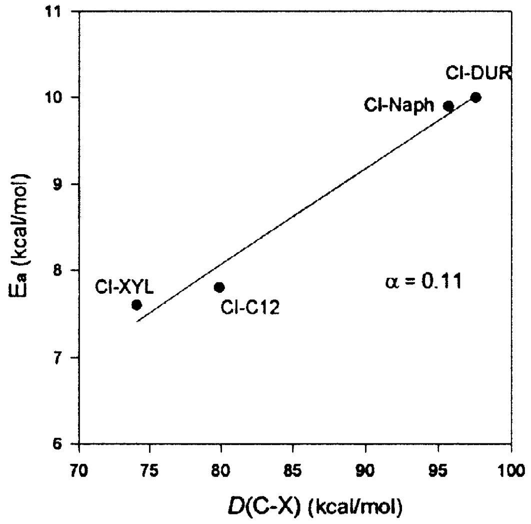


Fig 3

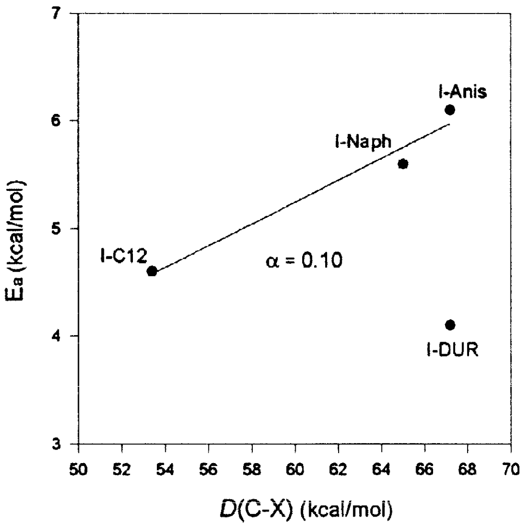


Fig 4

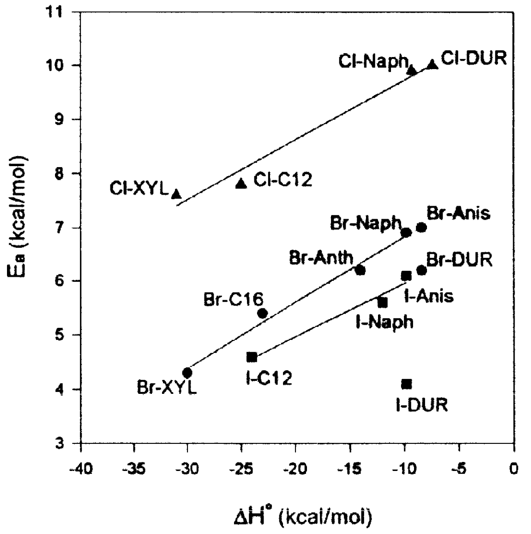


Table 3. Relative and absolute rate constants of dehalogenation; E_a and ΔH_o data

substrate (short notation)	t (°C)	k_{rel} (*vs.* relay compd.)	k_{abs} $M^{-1} s^{-1}$	E_a kcal/mol	ln A $M^{-1} s^{-1}$	ΔH° kcal/mol (from eq. 6)
1-Br-naphth.	80	1.98 (a)	7.92×10^6	6.9	25.7	-9.8
(Br-Naph)	93	1.93 (a)	1.10×10^7			
	110	1.92 (a)	1.67×10^7			
9-Br-anthracene	70	11.3 (a)	3.30×10^7	6.2	26.5	-14
(Br-Anth)	80	11.0 (a)	4.40×10^7			
	95	10.4 (a)	6.18×10^7			
α-Br-p-xylene	80	44.1 (b)	3.49×10^8	4.3	25.8	-30
(Br-XYL)	95	37.1 (b)	4.26×10^8			
	110	33.7 (b)	5.63×10^8			
1-Br-hexadecane	69	7.61 (b)	4.29×10^7	5.4	25.5	-23
(Br-C16)	89	6.75 (b)	6.65×10^7			
	110	5.98 (b)	9.99×10^7			
3-Br-durene	71	1.04 (b)	6.22×10^6	6.2	24.8	-8.4
(Br-DUR)	91	1.00 (b)	1.04×10^7			
	110	0.952 (b)	1.59×10^7			
1-I-naphth.	70	1.57 (c)	4.47×10^8	5.6	28.1	-12
(I-Naph)	95	1.80 (c)	7.67×10^8			
	110	1.90 (c)	1.07×10^9			
4-I-anisole	71	0.97 (c)	2.83×10^8	6.1	28.4	-9.8
(I-Anis)	87	1.10 (c)	4.24×10^8			
	106	1.25 (c)	6.51×10^8			
3-I-durene	71	3.31 (d)	1.46×10^9	4.1	27.1	-9.8
(I-DUR)	91	2.90 (d)	2.00×10^9			
	110	2.54 (d)	2.72×10^9			
1-I-dodecane	70	4.90 (d)	2.11×10^9	4.6	28.2	-24
(I-C12)	91	4.56 (d)	3.15×10^9			
	110	4.24 (d)	4.29×10^9			
α-Cl-p-xylene	71	0.614 (b)	3.67×10^6	7.6	26.2	-31
(Cl-XYL)	91	0.649 (b)	6.75×10^6			
	110	0.683 (b)	1.14×10^7			
1-Cl-naphth.	82	0.0195 (a)	8.24×10^4	9.9	25.4	-9.3
(Cl-Naph)	91	0.0216 (a)	1.17×10^5			
	110	0.0269 (a)	2.34×10^5			
1-Cl-dodecane	71	18.3 (e)	9.74×10^5	7.8	25.2	-25
(Cl-C12)	87	16.7 (e)	1.70×10^6			
	110	13.6 (e)	3.18×10^6			
3-Cl-durene	73	1.30 (e)	7.54×10^4	10.0	25.8	-7.4
(Cl-DUR)	91	1.39 (e)	1.63×10^5			
	110	1.32 (e)	3.09×10^5			

Relay compounds: a) *o*-Br-anisole; b) 1-Br-naphthalene; c) α-Br-p-xylene; d) 1-I-naphthalene; e) 1-Cl-naphthalene.

However, it should be reminded that a Sn-X bond of *different* energy is formed in the three series of organic halides. If the D(R-X) term of eq. 2 is replaced by the ΔH° of the appropriate reactions, as expressed in eq. 6,[3] a more generally useful formulation of the Evans-Polanyi equation is obtained.

$$\text{R-X} + \text{Bu}_3\text{Sn}^\bullet \rightarrow \text{Bu}_3\text{Sn-X} + \text{R}^\bullet \qquad \Delta H^{\circ} = D(\text{R-X}) - D(\text{Sn-X}) \qquad (6)$$

To this end, the BDE of the Bu_3Sn-X products is required. Unfortunately, these values are not available. The D(Sn-Br) of Me_3Sn-Br is known to be equal to 91.3 kcal/mol,[4b] which can be reasonably assumed to hold for the tri*butyl*-analogue. A $\Delta_fH_{298}(Me_3Sn\cdot)$ equal to 31.6 kcal/mol can be deduced from thermochemical data (see Experimental) which, together with the available $\Delta_fH_{298}(Me_3SnI)$ (-19.7 kcal/mol),[4c] gives a D(Sn-I) value of 77 kcal/mol for Me_3Sn-I. Since the Δ_fH_{298} value for Me_3SnCl is not available, a D(Sn-Cl) of ca. 105 kcal/mol for Me_3Sn-Cl was tentatively extrapolated from the parallel trend of the D(Si-X) values of the *silyl* derivatives Me_3Si-I, Me_3Si-Br, Me_3Si-Cl, corresponding to 77, 94, and 113 kcal/mol, respectively.[4]

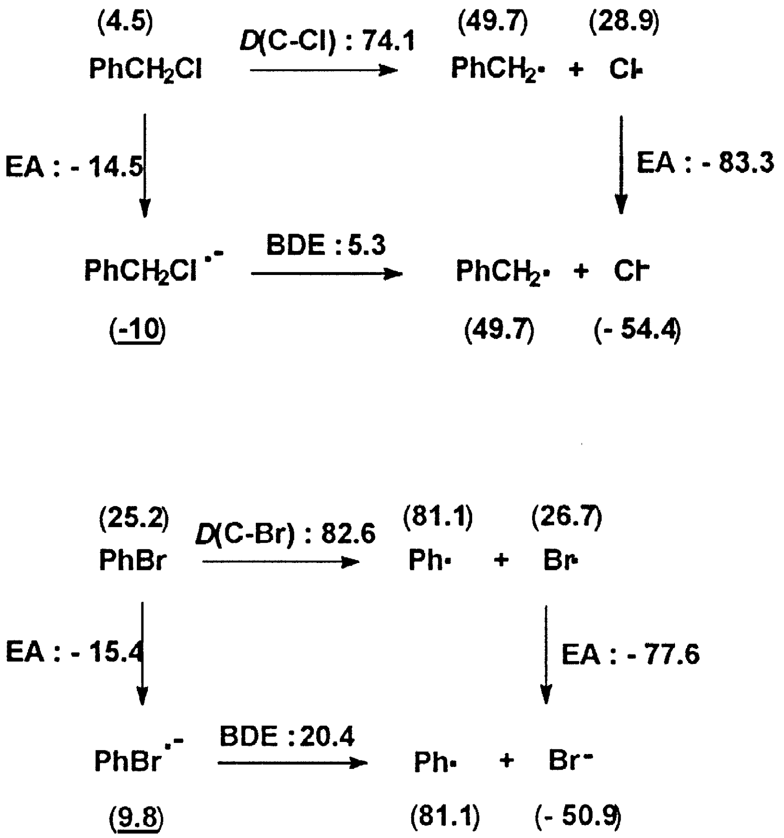
Correlation of E_a vs. ΔH°. The D(Sn-X) for Bu_3Sn-I, Bu_3Sn-Br, Bu_3Sn-Cl, *evaluated* above as 77, 91, and 105 kcal/mol, allow calculation of the ΔH° value for the dehalogenation reaction for *all* the selected organic halides, as $\Delta H^{\circ} = D(\text{R-X}) - D(\text{Sn-X})$. The ΔH° values obtained in this way are reported in Table 3 and are plotted *vs.* the corresponding E_a values in Fig. 4. The strong similarity of the slope of the correlations of the iodo-, bromo-, and chloroderivatives, already emerging from the separate plots of Figs 1-3, if allowance is made for the different number of experimental points of the three series,[14] is obviously shown again by Fig 4, even though in a clearer way. The similarity of the slopes suggests a comparable degree of halogen transfer in the TS, regardless the nature of the halogen. On varying the nature of the halogen, one could have expected effects associated with the different polarity of the C-X bond on the reactivity of the tin-induced dehalogenation. Being the tin radical electrophilic,[2] a slightly more pronounced selectivity of substrate could have been anticipated on going from the chloro- to the bromo- and to the iododerivatives, as due to a progressively 'later' TS for a gradually less electronegative halogen atom. No appreciable effect is instead observed.

One electron more! A review by Chanon *et al.*[15] commented on the effect that addition of one electron to, or removal of one electron from, an organic molecule may have on its reactivity. We calculate how strong can be the weakening effect on the energy of a C-X bond from addition of one electron to the RX compound. It is known that addition of one electron to aryl halides, followed by cleavage of the C-X bond (eqs. 7 and 8), represents the beginning of the aromatic $S_{RN}1$ process of nucleophilic substitution.[16]

$$\text{ArX} \xrightarrow{e^-} \text{ArX}^{\bullet-} \qquad (7)$$

$$\text{ArX}^{\bullet-} \rightarrow \text{Ar}^\bullet + \text{X}^- \qquad (8)$$

For a calculation of the BDE of the C-X bond in a radical anion, the following thermochemical cycles are used, where knowledge of the gas phase electron affinity (EA) of the atoms[17,18] and of the neutral precursors involved is required. The latter EA values are obtained from electron transmission spectroscopy,[19] but they are known only for PhBr and $PhCH_2Cl$ among the substrates investigated here. In the corresponding thermochemical cycles (Scheme 2) all data are given in kcal/mol, including the EA's values, and the bracketed data are the enthalpies of formation of the species; underlined values are those calculated here for the first time. From both cycles it can be appreciated how dramatically the energy of the C-X bond is decreased on the addition of one electron. In the case of PhBr$^{\bullet-}$, the BDE is lowered to about one-fourth; the decrease is even stronger with $PhCH_2Cl$, and approaches one-fifteenth! These unprecedented thermochemical evaluations of the energy of the C-X bond in a radical anion are in keeping with kinetic evidence concerning the rate of fragmentation of the same bonds in solution. According to Savéant, in fact, transfer of one electron to PhBr represents an example of a *stepwise* mechanism of reductive cleavage of an organic halide.[20] This process involves the intermediacy of the PhBr$^{\bullet-}$ species, whose subsequent rate of cleavage of the C-Br bond is estimated to be of the order of 10^8 s^{-1}.[20b,21] Conversely, benzyl halides represent examples of a *concerted* electron-transfer/bond-breaking mechanism, proceeding without the intermediacy of the radical anion.[20a] Our evaluation of an energy of ca. 20 kcal/mol for the C-Br bond of PhBr$^{\bullet-}$ supports the existence of this species as a reactive intermediate endowed with a finite, even though short, lifetime (ca. 10^{-9} s). Conversely, a C-Cl energy of only 5 kcal/mol for $PhCH_2Cl^{\bullet-}$ corroborates the idea that $PhCH_2Cl$ breaks apart while the electron is transferred to it, without any finite lifetime for the radical anion.[22]



Scheme 2

Experimental

Materials. All the compounds were commecially available. 4-Iodoanisole was synthesized by following 'method *a*' described in a previous publication.[23] The halodurenes were available from previous investigations.[23,24] The synthesis of α-iodo-*p*-xylene was attempted, in order to increase the number of iodo-derivatives investigated. Unfortunately, Finkelstein I/Br exchange on α-bromo-*p*-xylene gave a solid product which quickly decomposed to tars in air. Reaction solvents benzene or toluene were dried over sodium wires.

Competition Experiments of Dehalogenation. A solution of a reference substrate (R'X; 1 mmol), a competing substrate (RX; 1 mmol), a GC internal standard (in general biphenyl; 0.5 mmol), AIBN (0.1 mmol), Bu_3SnH (0.5 mmol) in 3 ml of dry benzene (or toluene) was placed under nitrogen, and heated at a suitable temperature in a thermostated bath for 4-6 h. An aliquot was removed, diluted and analyzed by GC for the determination of the yield of the reduced products (R'H and RH). GC response factors for the reduced compounds relative to the internal standard were determined and used to correct the raw GC data. All experiments were run at least in duplicate, and typical GC errors were ±3%. Relative reactivities ($k_{rel} = k_{RX}/k_{R'X}$) were reckoned from use of the standard integrated formula for competitive reactions,[2,25] while absolute rate constants were gauged by multiplying these k_{rel} data by the known rate constant of dehalogenation of the relay compound R'X (either 2-bromobenzonitrile, 1.6×10^7 M^{-1} s^{-1}, or 3-bromoanisole, 4.0×10^6 M^{-1} s^{-1})[2] at 80 °C. When the competition reactions were done at temperatures other than 80 °C, 3-bromoanisole was in general employed as the standard substrate (toluene was the solvent, in this case), and its absolute rate constant of dehalogenation at each specific temperature was obtained from the Arrhenius equation, being 7.0 kcal/mol and 25.3 M^{-1} s^{-1} its E_a and ln A parameters, respectively.[26]

Determination of the Energy of Activation. From the rate constants at the various temperatures (three temperatures in each case, in the 70 - 110 °C interval), the E_a value of the substrates was obtained from the Arrhenius equation (Table 3). Correlation coefficients *r* were good (0.997-0.999). Correlations of E_a data with *D*(C-X) data for the bromo-, chloro- and iododerivatives are shown in Figs 1-3. Calculation of the ΔH^o of the reaction as *D*(R-X) - *D*(Sn-X) was instead required for a plot bound to include *all* the haloderivatives together (Table 3 and Fig. 4).

Determination of Thermochemical Parameters. Equation 5 was employed in order to calculate the required data (see text and Table 2). Apart from the BDE data of the literature and the enthalpies of formation of neutral and radical species (that are always referred to the gas-phase) reported in Table 2, other useful data are the following. The $\Delta_f H_{298}(X\cdot)$ of the halogens (in kcal/mol) are 28.9 (Cl·), 26.7 (Br·), 25.5 (I·),[4b] while the corresponding data for H· and Et· are 52.1 and 28.4, respectively.[4b,d] A $\Delta_f H_{298}(Me_3Sn\cdot)$ of 31.6 kcal/mol was reckoned from eq. 5, being available the $D(Me_3Sn\text{-}Me)$ (71.0 kcal/mol),[4b] the $\Delta_f H_{298}(Me\cdot)$ and the $\Delta_f H_{298}(Me_4Sn)$ (34.9 and -4.54 kcal/mol, respectively) values.[4b,c] The EA values derive from electron transmission spectroscopy data of the literature;[17-19] they were expressed in eV (1 eV is 23.06 kcal/mol) but are reported here in kcal/mol (1 cal is 4.18 J).

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