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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

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Abstract: The energy of activation (E_a) of the dehalogenation reaction induced by Bu₃Sn[•] 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. © 1998 Elsevier Science Ltd. All rights reserved.

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.

 $\begin{array}{ccc} AIBN & RX \\ Bu_3SnH \rightarrow & Bu_3Sn^* \rightarrow & Bu_3SnX + R^* \end{array}$ (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.

$$E_a = \alpha D(R-X) + \cos t$$
 (2)

The values of D(R-X) required to establish the correlation have been obtained from $\Delta_f H_{298}$ 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.

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

Bu₃SnH/AIBN R-X / R'-X \rightarrow R-H / R'-H (+ Bu₃SnX) (3) k_{RX} R-X + Bu₃Sn^{*} \rightarrow R* + Bu₃SnX R* + Bu₃SnH \rightarrow R-H + Bu₃Sn* $k_{R'X}$ R'-X + Bu₃Sn^{*} \rightarrow R'* + Bu₃SnX R'* + Bu₃SnH \rightarrow R'-H + Bu₃Sn* 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 Bu₃Sn' at 80 °C was known, was used as the relay compound. These substrates were 2-bromobenzonitrile ($k_{R'X} = 1.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) and 3-bromoanisole ($k_{R'X} = 4.0 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$).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 view¹ that the dehalogenation of the substrate by Bu₃Sn^{*} 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.

$$\mathbf{R}^* + \mathbf{R}^* \cdot \mathbf{X} \to \mathbf{R}^{**} + \mathbf{R} \cdot \mathbf{X}$$
(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

the TS, and the more the homolytic process will discriminate among different substrates as a function of their C-X bond energy.

RX	$k (in M^{-1} s^{-1})$	RX	k (in $M^{-1} s^{-1}$)	
4-iodoanisole	8.8 x 10 ⁸	E-4-bromo-4-octene	4.9 x 10 ⁶	
1-iodonaphthalene	6.1 x 10 ⁸	3-bromoanisole	4.0 x 10 ⁶	
α-bromo-p-xylene	3.4 x 10 ⁸	4-bromoanisole	2.4 x 10 ⁶	
2-bromobenzonitrile	1.6 x 10 ⁷	4-bromobiphenyl	3.2 x 10 ⁶	
1-bromonaphthalene	7.8 x 10 ⁶	3-chlorodurene	1.1 x 10 ⁵	
2-bromonaphthalene	4.5 x 10 ⁶	a-chloro-p-xylene	5.0 x 10 ⁶	
1-bromooctane	5.8 x 10 ⁷	1-chlorododecane	1.3 x 10 ⁶	
β-bromostyrene	2.7 x 10 ⁶	benzoyl chloride	2.4×10^{7}	

Table 1. Rates of dehalogenation of RX compound by Bu₃Sn^{*} in benzene at 80 °C (data in *italics* are from ref. 2).

In order to test these predictions, reliable D(C-X) values are required for the organic halides of interest. In fact, only a few of them are reported. For example, the ethyl derivatives have $D_{298}(Et-X)$ values of 107.7, 79.9, 68.5, and 53.4 kcal/mol for X equal to F, Cl, Br, and I, respectively.⁴ The BDE's of the benzylic halides PhCH₂Cl, PhCH₂Br, and PhCH₂I are 72.2, 57.5, and 48.2 kcal/mol, respectively, but these data are rather old.^{4c} Equally old are the $D_{298}(Ph-X)$ values of the simple phenyl halides, PhF, PhCl, PhBr, and PhI, reported as 125.7, 95.7, 80.5, and 65.4 kcal/mol, respectively.^{4c} While these numbers confirm that sp³ C-X bonds are weaker than the corresponding sp² C-X ones, the reliability of some data is not high,^{4c} and above all there are no data for more complex aromatic or vinylic structures. Consequently, any comment on the reactivity trends shown in Table 1 is presently grounded on *likely* data, without an exhaustive quantitative information behind. Such a lack of data has prompted our attempt to obtain the BDE's for a wider series of organic halides.

Calculation of D(R-X) values. BDE data can be obtained from the use of relationships such as that of eq. 5, where the gas-phase enthalpies of formation of radicals and neutral species are employed.

$$D_{298}(R-X) = \Delta_{f} H_{298}(R\cdot) + \Delta_{f} H_{298}(X\cdot) - \Delta_{f} H_{298}(RX)$$
(5)

Whenever using eq. 5 for PhX compounds, the recent determination⁵ of $\Delta_{\rm f} H_{298}(\rm Ph^{-})$ (as 81.1 kcal mol⁻¹), which shifts by ca. 2.5 kcal/mol upward the previously accepted enthalpy of formation of the phenyl radical, compels to reset all the BDE values that were derived from the previous value. By using the new $\Delta_{\rm f} H_{298}(\rm Ph^{-})$ value in eq. 5, along with the well known enthalpies of formation of the pertinent halogen atom and neutral

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 $\Delta_{f}H_{298}$ (PhCH₂·) 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, and the β C-H bond as 0.3 kcal/mol weaker. Since the D_{298} (C-H) of benzene is 113.45 kcal/mol, 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 $\Delta_{f}H_{298}(H)$ (52.1 kcal/mol) and of $\Delta_{f}H_{298}$ (naphthalene) (35.99 kcal/mol), eq. 5 provides the $\Delta_{f}H_{298}(\alpha$ -naphthyl·) and $\Delta_{f}H_{298}(\beta$ -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 $\Delta_{f}H_{298}(\alpha$ bromonaphthalene) 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 $\Delta_{f}H_{298}(\alpha$ -bromonaphthalene) can be calculated to be equal to 40.9 kcal/mol.

R [Δ _f H ₂₉₈ (R·)]	Δ _f H ₂₉₈ (RH)	D ₂₉₈ (R-H)	Δ _f H ₂₉₈ (RX)	D ₂₉₈ (R-X) 97.6
phenyl [81.1]	19.75		PhC1 12.4	
			PhBr 25.2	82.6
			PhI 39.4	67.2
benzyl [49.7]	11.97	89.8	PhCH ₂ Cl 4.47	74.1
			PhCH ₂ Br 15.2	61.2
			PhCH ₂ I 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
ethenyi [71.7]	12.55	111.2	Cl-ethene 9.10	91.5
			Br-ethene 18.93	79.5
Me ₃ Sn [31.6]	-	-	Me ₃ SnCl -	107 (extr) ^b
			Me ₃ SnBr -33.0	91.3
			Me ₃ SnI -19.7	76.8

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

"Literature data are from refs. 4-9, and are in kcal/mol "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 $\Delta_{f}H_{298}$ value for 9-anthryl- radical results to be equal to 112.5 kcal/mol, using the known $\Delta_{f}H_{298}(anthracene)$ (i.e., 55.0 kcal/mol) and $\Delta_{f}H_{298}(H)$ values.⁴ The $\Delta_{f}H_{298}(9$ -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 $\Delta_{f}H_{298}$ (CH₂=CH·) of 71.7 kcal/mol.⁹ Thus, knowledge of the $\Delta_{f}H_{298}$ (chloroethene) (9.10 kcal/mol) and $\Delta_{f}H_{298}$ (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 $\pm 0.2 - 0.4$ kcal/mol.

Energy of activation of the dehalogenation reaction. The energy of activation Ea for the dehalogenation induced by Bu₃Sn[•] 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 Bu₃Sn⁴ (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 Bu₃Sn[•] is calculated to be 7.0 kcal/mol (In 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 Ea and In 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 $\pm 0.4 - 0.8$ 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 Bu₃Sn^{*} 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 Bu₃Sn^{*} becomes faster as the C-X bond becomes weaker. The structure of the precursors can vary considerably without any major prejudice to 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-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.



substrate	t (°C)	le .	منځورونو ورونو ورونو م جا	rieren Kennen E	ln A	۵H°
(short notation)	•(-)	Krel (vs. relav	Kabs	Eg kcsl/mol	M ¹ s ⁻¹	kcal/mol
		compd.)	INT 2	Rouginor		(from eq. 6)
I-Br-naphth.	80	1.98 (a)	7.92x10 ⁶			
(Br-Naph)	93	1.93 (a)	1.10×10^7	6.9	25.7	-9.8
	110	1.92 (a)	1.67×10^{7}			
9-Br-anthracene	70	11.3 (a)	3.30x10 ⁷			
(Br-Anth)	80	11.0 (a)	4.40×10^{7}	6.2	26.5	-14
	95	10.4 (a)	6.18x10'			
α-Br-p-xylene	80	44.1 (b)	3.49x10 ⁸			
(Br-XYL)	95	37.1 (b)	4.26x10 ⁸	4.3	25.8	-30
	110	33.7 (b)	5.63x10 [*]			
1-Br-hexadecane	69	7.61 (b)	4.29x10 ⁷			
(Br-C16)	89	6.75 (b)	6.65x10 ⁷	5.4	25.5	-23
	110	5.98 (b)	9.99x10'			
3-Br-durene	71	1.04 (b)	6.22×10^{6}			
(Br-DUR)	9 1	1.00 (b)	1.04×10^{7}	6.2	24.8	-8,4
	110	0.952 (b)	1.59x10'			
1-I-naphth.	70	1.57 (c)	4.47x10 [*]			
(I-Naph)	95	1.80 (c)	7.67x10 ⁸	5,6	28.1	-12
	110	1.90 (c)	1.07x10 [°]			
4-I-anisole	71	0.97 (c)	2.83x10 ⁸			
(I-Anis)	87	1.10 (c)	4.24x10	6.1	28.4	-9.8
	106	1.25 (c)	6.51x10°			
3-I-durene	71	3.31 (d)	1.46x10 ⁹			
(I-DUR)	91	2.90 (d)	2.00x10 ⁹	4.1	27.1	-9.8
	110	2.54 (d)	2.72x10 [*]			
1-I-dodecane	70	4.90 (d)	2.11x10 ⁹			
(I-C12)	91	4.56 (d)	3.15x10 [°]	4.6	28.2	-24
	110	4.24 (d)	4.29x10 ^s			
α -Cl-p-xylene	71	0.614 (b)	3.67x10°			
(Cl-XYL)	91	0.649 (b)	6.75x10°	7.6	26.2	-31
	110	0.683 (b)	1.14x10'			
1-Cl-naphth.	82	0.0195 (a)	8.24x10 ⁴			
(Cl-Naph)	91	0.0216 (a)	1.17x10°	9.9	25.4	-9.3
	110	0.0269 (a)	2.34x10 ³			
1-Cl-dodecane	71	18.3 (e)	9.74x10 ⁵	_		4
(Cl-C12)	87	16.7 (e)	1.70x10°	7.8	25.2	-25
	110	13.6 (e)	3.18x10°			
3-Cl-durene	73	1.30 (e)	7.54x10 ⁴			
(CI-DUR)	91	1.39 (e)	1.63x10°	10.0	25.8	-7.4
	110	1.32 (e)	3.09x10'			

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

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.

$$R-X + Bu_3Sn^* \rightarrow Bu_3Sn-X + R^* \qquad \Delta H^* = D(R-X) - D(Sn-X)$$
(6)

To this end, the BDE of the Bu₃Sn-X products is required. Unfortunately, these values are not available. The D(Sn-Br) of Me₃Sn-Br is known to be equal to 91.3 kcal/mol,^{4b} which can be reasonably assumed to hold for the tributyl-analogue. A $\Delta_1 H_{298}(Me_3Sn\cdot)$ equal to 31.6 kcal/mol can be deduced from thermochemical data (see Experimental) which, together with the available $\Delta_1 H_{298}(Me_3SnI)$ (-19.7 kcal/mol),^{4c} gives a D(Sn-I) value of 77 kcal/mol for Me₃Sn-I. Since the $\Delta_1 H_{298}$ value for Me₃SnCl is not available, a D(Sn-Cl) of ca. 105 kcal/mol for Me₃Sn-Cl was tentatively extrapolated from the parallel trend of the D(Si-X) values of the *silyl* derivatives Me₃Si-I, Me₃Si-Br, Me₃Si-Cl, corresponding to 77, 94, and 113 kcal/mol, respectively.⁴

Correlation of E_a vs. ΔH° . The D(Sn-X) for Bu₃Sn-I, Bu₃Sn-Br, Bu₃Sn-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 I-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_{RN1} process of nucleophilic substitution.¹⁶

$$\begin{array}{c} e \\ ArX \xrightarrow{e} & ArX^{\bullet} \end{array}$$
(7)
$$ArX^{\bullet} \xrightarrow{} & Ar^{\bullet} + X^{\bullet} \end{array}$$
(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 PhCH₂Cl 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^{*}, the BDE is lowered to about one-fourth; the decrease is even stronger with PhCH₂Cl, 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^{*} 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.²⁰ Our evaluation of an energy of ca. 20 kcal/mol for the C-Br bond of PhBr^{*} 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 PhCH₂Cl^{*} corroborates the idea that PhCH₂Cl 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), Bu₃SnH (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, $1.6 \times 10^7 M^{-1} s^{-1}$, or 3-bromoanisole, $4.0 \times 10^6 M^{-1} s^{-1}$) 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.

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° 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 $\Delta_{\rm f}H_{298}(X\cdot)$ 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 $\Delta_{\rm f}H_{298}(Me_3Sn\cdot)$ of 31.6 kcal/mol was reckoned from eq. 5, being available the $D(Me_3Sn-Me)$ (71.0 kcal/mol),^{4b} the $\Delta_{\rm f}H_{298}(Me\cdot)$ and the $\Delta_{\rm f}H_{298}(Me_4Sn)$ (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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