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THEORETICAL MODELS FOR THE REDUCTION OF ARYLMETHYL HALIDES BY TRIORGANOTIN HYDRIDES*

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Two mechanistic pathways have been proposed for halogen atom transfer from the benzylic positions of halomethylarenes to triorganotin radicals. These are direct atom abstraction, which might involve an extremely polar transition state, and single electron transfer followed by bond cleavage. AM1 semi-empirical calculations have been utilized to model the rate-determining step of these processes. A wide range of related families of compounds have been studied, including substituted halomethylbenzenes, selected halomethyl-substituted polycyclic aromatic hydrocarbons and oxygen- and nitrogen-containing chloromethyl-substituted heteroaromatic systems. Although these calculations are relatively simple, the present results corroborate the view that chlorine and bromine atom transfer from the benzylic position to triorganotin radicals involves a direct atom abstraction in the rate-determining step whereas reduction of the corresponding iodides proceeds via an electron-transfer mechanism.

INTRODUCTION

$$\text{Initiator} \rightarrow \text{In}\cdot$$

$$R'_3\text{SnH} + \text{In}\cdot \rightarrow R'_3\text{Sn}\cdot + \text{InH}$$

$$R'_3\text{Sn}\cdot + \text{RX} \quad \overset{\text{RDS}}{\qquad} \quad R'_3\text{SnX} + \text{R}\cdot$$

$$R'_3\text{SnH} + \text{R}\cdot \rightarrow R'_3\text{Sn}\cdot + \text{RH}$$

Scheme 1. Traditional mechanism

The use of trialkyl- or triaryltin hydrides to reduce organic halides has become a relatively common reaction of great synthetic utility [equation (1)].[1] The

$$\text{R}-\text{X} + R'_3\text{SnH} \xrightarrow{\text{Initiator}} \text{R}-\text{H} + R'_3\text{SnX} \qquad (1)$$

free-radical nature of this overall process was not originally recognized;[2] however, Kuivila and co-workers[3,4] provided extensive evidence for a traditional atom transfer mechanism as shown in Scheme 1. Grady *et al.*,[5] in an investigation of substituent effects in the reduction of substituted benzyl chlorides by tri-*n*-butyltin hydride, observed a large positive ρ value. By analogy with other (i.e. hydrogen) atom-transfer processes, this would suggest appreciable charge separation in the transition state for the reaction.[6] A resonance description for this is

$$\underset{\text{I}}{\text{R}-\text{X}\ \cdot\text{Sn}} \leftrightarrow \underset{\text{II}}{\text{R}\cdot\ \text{X}-\text{Sn}} \leftrightarrow \underset{\text{III}}{\text{R}:^{-}\dot{\text{X}}\ {}^{+}\text{Sn}}$$

Blackburn and Tanner[7] re-examined and significantly extended this latter study. They found optimum correlation with σ^{-}, rather than σ, constants. They also observed, as might be predicted, a lessened substituent dependence in the corresponding reduction of substituted benzyl bromides. In the case of the substituted benzyl iodides, however, a much larger substituent dependence was discovered. This is not consistent with direct atom transfer since the weak carbon—iodine bond should be associated with a more exothermic (early transition state) process. Possible changes in mechanism were suggested. One of these, a single

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$$\text{Initiator} \rightarrow \text{In}\cdot$$

$$R'_3SnH + In\cdot \rightarrow R'_3Sn\cdot + InH$$

$$R'_3Sn\cdot + RX \rightarrow R'_3Sn^+ + [RX]^{-\cdot}$$

$$[RX]^{-\cdot} \rightarrow R\cdot + X^-$$

$$R'_3SnH + R\cdot \rightarrow R'_3Sn\cdot + RH$$

Scheme 2. Electron-transfer (Blackburn and Tanner) mechanism

electron-transfer (SET) process is given in Scheme 2 (for an overview of this type of reaction, see Ref. 8). Further support for a mechanistic dichotomy between iodides vs bromides and chlorides in hydride reductions was found by Kochi *et al.*[9]

Influenced in part by this suggested dualilty of mechanism, we have investigated the reaction of several systems of halomethyl derivatives of conjugated molecules with triphenyltin hydride. These include chloromethyl polycyclic alternant hydrocarbons,[10] iodomethyl polycyclic alternant hydrocarbons,[11] chloromethyl oxygen-containing heterocycles,[12] and, most recently, chloromethyl nitrogen-containing heterocycles.[13] Attempts to correlate relative reactivity with calculated Π energy differences at the SCF (PPP) level have met with varying degrees of success. The present study was designed to make use of more sophisticated semi-empirical all-valence-electron calculations (AM1) to correlate existing data and hopefully provide an insight into the proposed dichotomy of mechanism.

EXPERIMENTAL AND RESULTS

Calculations were performed on ground-state, radical anionic, carbanionic and radical species for all compounds. A customized version of AMPAC (QCPE 506 Version 2.1),[14] amended to run on a DEC VAX 11-780/FPS-264, was used to carry out the computations. Input files were generated and the geometries optimized using the program PCMODEL (Serena Software, Bloomington, IN, USA). Local energy minima were found when the Cl—C-α—C-1—C-2 dihedral angles were *ca* 90° (carbon—halogen bonds in planes orthogonal to the plane of the rings). All geometries were further optimized within the AMPAC subroutines. All energies were calculated at the restricted Hartree–Fock (RHF) level. A second set of computations was attempted at the unrestricted Hartree–Fock (UHF) level. The UHF results for certain compounds were deemed unsatisfactory in that they predicted unrealistically high spin states for known singlet, ground-state molecules.[15] The Austin Model 1 (AM1) was selected as the parametric quantum mechanical molecular model for comparison of reactive species.[16,17] This approach is among the most frequently cited of those molecular orbital methods used to correlate problems of chemical reactivity.

AM1[14,16,17]-calculated relative total energy differences (the unsubstituted benzyl halide was used as a reference compound) between a presumed transition state and starting material were correlated with logarithms of the relative rates of halogen atom transfer. The goodness of fit (correlation coefficient) of these relationships was used in the current investigation as the criterion for suitability of the model. Correlations based on benzylic radical or anionic intermediates ($\Delta E_T^r, \Delta E_T^a$) reflect a direct atom-abstraction process, whereas correlations based on a radical anion model (ΔE_T^{ra}) reflect an electron-transfer mechanism:

$$\Delta E_T^r = E_T(Ar\dot{C}H_2) - E_T(ArCH_2X)$$
$$\Delta E_T^a = E_T(Ar\ddot{C}H_2) - E_T(ArCH_2X)$$
$$\Delta E_T^{ra} = E_T(ArCH_2X)^{-\cdot} - E_T(ArCH_2X)$$

The results of the correlations for the systems studied are given in Table 1. Individual rate data and calculated quantities are presented as supplementary material in Tables 2–8.

The positive ρ values obtained in the investigation of substituent effects in halogen atom transfer from substi-

Table 1. Correlation coefficients (r) and slopes of correlations of logarithms of relative rates of halogen atom transfer versus AM1-calculated parameters

	Model								
	Radical		Carbanion		Radical anion		π-LUMO		
System	*r*	Slope	*r*	Slope	*r*	Slope	*r*	Slope	Ref.
Substituted benzyl chlorides	0·225	−0·495	0·912	−0·421	0·910	−0·424	0·921	−0·408	7
Substituted benzyl bromides	0·870	−10·029	0·954	−0·185	0·959	−0·220	0·975	−0·219	7
Substituted benzyl iodides	0·251	−31·447	0·922	−0·911	0·952	−1·145	0·963	−1·222	7
Chloromethylhomoarenes	0·941	−4·655	0·960	−1·433	0·912	−1·274	0·898	−1·187	10
Iodomethylhomoarenes	0·443	−1·563	0·836	−0·457	0·942	−0·483	0·964	−0·451	11
Nitrogen-heteroarylmethyl chlorides	0·085	−0·206	0·937	−1·058	0·896	−0·858	0·869	−0·871	13
Oxygen-heteroarylmethyl chlorides	0·363	0·398	0·778	−0·619	0·716	−0·570	0·639	−0·470	12

Table 2. Relative reactivities[a] and AM1-calculated parameters for substituted benzyl chlorides[b]

Substituent	k_{rel}	$\Delta\Delta E_T^r$	$\Delta\Delta E_T^a$	$\Delta\Delta E_T^{ra}$	E_{LUMO}
p-*t*-Bu	0·97 ± 0·01	0·006	−0·060	−0·050	0·025
p-Me	1·04 ± 0·01	0·004	−0·036	−0·032	−0·015
m-Me	1·08 ± 0·01	0·005	0·010	0·006	0·029
H	1·00	0·000	0·000	0·000	0·000
p-Ph	1·33 ± 0·04	—	−0·455	−0·471	−0·415
p-F	1·17 ± 0·01	−0·019	−0·263	−0·284	−0·336
p-Cl	1·45 ± 0·04	−0·010	−0·354	−0·346	−0·340
m-F	1·29 ± 0·01	−0·005	−0·315	−0·283	−0·300
m-Cl	1·57 ± 0·01	−0·008	−0·321	−0·300	−0·273
m-CF_3	1·64 ± 0·01	−0·022	−0·560	−0·599	−0·631
p-CO_2Et	1·87 ± 0·03	−0·010	−0·855	−0·812	−0·748
m-CN	1·87 ± 0·03	−0·013	−0·496	−0·581	−0·664
p-CN	2·78 ± 0·16	−0·011	−0·817	−0·779	−0·810

[a] From Ref. 7.

[b] Benzyl chloride was used as a reference. All energies are in eV.

Table 3. Relative reactivities[a] and AM1-calculated parameters for substituted benzyl bromides[b]

Substituent	k_{rel}	$\Delta\Delta E_T^r$	$\Delta\Delta E_T^a$	$\Delta\Delta E_T^{ra}$	E_{LUMO}
p-Me	0·94 ± 0·03	0·004	−0·036	−0·017	−0·005
m-Me	0·97 ± 0·01	0·005	0·010	0·010	0·030
H	1·00	0·000	0·000	0·000	0·000
p-Br	1·20 ± 0·01	−0·008	−0·466	−0·395	−0·382
m-F	1·13 ± 0·01	−0·004	−0·314	−0·259	−0·274
m-Br	1·15 ± 0·01	−0·009	−0·344	−0·297	−0·279
p-CO_2Et	1·31 ± 0·04	−0·007	−0·853	−0·711	−0·675
p-CN	1·48 ± 0·06	−0·009	−0·815	−0·691	−0·739

[a] From Ref. 7.

[b] Benzyl bromide was used as a reference. All energies are in eV.

Table 4. Relative reactivities[a] and AM1-calculated parameters for substituted benzyl iodides[b]

Substituent	k_{rel}	$\Delta\Delta E_T^r$	$\Delta\Delta E_T^a$	$\Delta\Delta E_T^{ra}$	E_{LUMO}
H	1·00	0·000	0·000	0·000	0·000
m-Cl	2·12 ± 0·09	−0·006	−0·320	−0·252	−0·220
m-F	1·81 ± 0·03	−0·002	−0·312	−0·247	−0·248
p-Cl	1·81 ± 0·01	−0·008	−0·352	−0·284	−0·270
p-CN	7·29 ± 0·32	−0·005	−0·811	−0·642	−0·667
p-CO_2Et	4·36 ± 0·09	−0·003	−0·848	−0·654	−0·604
p-Ph	1·37 ± 0·12	—	−0·454	−0·284	−0·275
p-Me	0·92 ± 0·02	−0·004	−0·036	−0·010	−0·004

[a] From Ref. 7.

[b] Benzyl iodide was used as a reference. All energies are in eV.

Table 5. Relative reactivities[a] and AM1-calculated parameters for chloromethylhomoarenes[b]

Compound	k_{rel}	$\Delta\Delta E_T^r$	$\Delta\Delta E_T^a$	$\Delta\Delta E_T^{ra}$	E_{LUMO}
Benzyl chloride	1·00	0·000	0·000	0·000	0·000
1-Chloromethylnaphthalene	1·88 ± 0·11	-0·046	-0·436	-0·545	-0·436
2-Chloromethylnaphthalene	3·29 ± 0·48	0·028	-0·415	-0·484	-0·415
1-Chloromethylanthracene	3·79 ± 0·24	-0·077	-0·769	-0·987	-0·769
9-Chloromethylanthracene	7·95 ± 0·20	-0·284	-1·095	-1·099	-1·095
9-Chloromethylphenanthrene	38·68 ± 2·19	-0·032	-0·640	-0·736	-0·640

[a] From Ref. 10.
[b] Benzyl chloride was used as a reference. All energies are in eV.

Table 6. Relative reactivities[a] and AM1-calculated parameters for iodomethylhomoarenes[b]

Compound	k_{rel}	$\Delta\Delta E_T^r$	$\Delta\Delta E_T^a$	$\Delta\Delta E_T^{ra}$	E_{LUMO}
Benzyl iodide	1·000	0·000	-0·000	0·000	0·000
2-Iodomethylnaphthalene	1·24 ± 0·03	0·022	-0·368	-0·294	-0·365
1-Iodomethylnaphthalene	1·42 ± 0·02	-0·053	-0·496	-0·395	-0·450
9-Iodomethylphenanthrene	1·39 ± 0·03	-0·048	-0·656	-0·561	-0·547
2-Iodomethylanthracene	2·27 ± 0·11	+0·008	-0·623	-0·743	-0·839
1-Iodomethylanthracene	2·44 ± 0·10	-0·091	-0·782	-0·786	-0·874

[a] From Ref. 11.
[b] Benzyl iodide was used as a reference. All energies are in eV.

Table 7. Relative reactivities[a] and AM1-calculated parameters for nitrogen-containing chloromethylheteroarenes[b]

Compound	k_{rel}	$\Delta\Delta E_T^r$	$\Delta\Delta E_T^a$	$\Delta\Delta E_T^{ra}$	E_{LUMO}
2-Chloromethylpyridine	1·38 ± 0·09	0·098	0·216	-0·198	-0·306
3-Chloromethylpyridine	1·12 ± 0·08	-0·050	-0·320	-0·318	-0·361
4-Chloromethylpyridine	1·43 ± 0·08	-0·012	-0·306	-0·395	-0·280
2-Chloromethylquinoline	3·49 ± 0·33	0·157	-0·665	-0·581	-0·719
3-Chloromethylquinoline	2·92 ± 0·07	-0·026	-0·719	-0·634	-0·765
4-Chloromethylquinoline	5·08 ± 0·08	-0·018	-0·776	-0·837	-0·808
5-Chloromethylquinoline	3·43 ± 0·07	-0·038	-0·740	-0·667	-0·787
6-Chloromethylquinoline	2·11 ± 0·08	0·012	-0·687	-0·562	-0·745
7-Chloromethylquinoline	3·19 ± 0·04	-0·158	-0·850	-0·722	-0·732
8-Chloromethylquinoline	2·50 ± 0·04	-0·071	-0·729	-0·594	-0·774

[a] From Ref. 13.
[b] Benzyl chloride was used as a reference. All energies are in eV.

Table 8. Relative reactivities[a] and AM1-calculated parameters for oxygen-containing chloromethylheteroarenes[b]

Compound	k_{rel}	$\Delta\Delta E_T^r$	$\Delta\Delta E_T^a$	$\Delta\Delta E_T^{ra}$	E_{LUMO}
3-Chloromethylfuran	3·45 ± 0·45	-0·251	-0·006	-0·092	0·1000
4-Chloromethylfuran	0·54 ± 0·09	-0·183	0·190	0·433	0·260
3-Chloromethylbenzofuran	4·15 ± 0·06	0·085	-0·739	-0·448	-0·685
4-Chloromethylbenzofuran	1·80 ± 0·06	-0·522	0·015	-0·248	-0·542
1-Chloromethyldibenzofuran	2·91 ± 0·12	-0·012	-0·542	-0·384	-0·636
2-Chloromethyldibenzofuran	3·41 ± 0·09	0·040	-0·666	-0·709	-0·723
3-Chloromethyldibenzofuran	2·32 ± 0·06	0·008	-0·514	-0·334	-0·596
1-Chloromethyldibenzo-*p*-dioxin	2·09 ± 0·05	-0·029	-0·347	-0·493	-0·333
2-Chloromethyldibenzo-*p*-dioxin	2·16 ± 0·04	-0·001	-0·402	-0·511	-0·454

[a] From Ref. 12.
[b] Benzyl chloride was used as a reference. All energies are in eV.

tuted benzylic systems to triorganotin radical were attributed to the greater contribution of canonical form III (shown above) to the hybrid description of the transition state.[5,7] This is indicative of an appreciable negative charge development at the benzylic carbon in the transition state for direct atom abstraction.[5,7] In keeping with the above observation, it has proved fruitful to utilize a benzylic carbanion to model chlorine atom abstraction by triphenyltin radical from chloromethylhomoarenes[10] and chloromethylheteroarenes.[11] This approach was adopted in this work. Correlations based on a carbanion model were much superior to those based solely on a radical model (see Table 1) for most of the systems investigated. This finding is in agreement with the view that there is an appreciable charge separation in the transition state of halogen atom transfer to triorganotin radicals.[5,7,10,12,13] The sole exception was the series of chloromethylhomoarenes. This was not completely unexpected and may be viewed as a result of the alternant nature of these benzenoid systems. There exists a parallelism of calculated energies for the carbocations, radicals and carbanions derived from such systems.[18]

Substituted benzyl halides

With substituted benzyl chlorides (thirteen compounds) and bromides (eight compounds), the carbanion and radical anion models gave equally good correlations. While either of these correlations is good, aditional experimental evidence[9] would favor the direct atom-abstraction mechanism for these systems. It should be pointed out that there is an apparent parallelism between radical anion- and carbanion-calculated energy differences. For the substituted benzyl chlorides and bromides, the correlation coefficients obtained were 0·993 and 0·997, respectively.

For the substituted benzyl iodides (eight compounds) the radical anion model proved to be superior. The correlation coefficients for the radical anion model and carbanion model were 0·952 and 0·922, respectively. This tends to support Blackburn and Tanner's view[7] that iodine atom transfer from substituted benzyl iodides to triorganotin radicals proceeds with an electron-transfer mechanism rather than by direct atom abstraction.

Halomethylhomoarenes

Soppe-Mbang and Gleicher[10] reported an excellent correlation (0·990) when the logarithms of the relative rates of chlorine atom transfer from a series of six chloromethylhomoarenes were plotted against SCF–PPP[19,20]-calculated energy differences between the benzylic carbanions and parent arenes. They rationalized these findings on the basis of a substantial negative charge development in the transition state of the direct atom abstraction.[10] Workers in the same laboratory have shown that iodine atom transfer from six iodomethylhomoarenes to triphenyltin radicals has a smaller dependence on substrate structure.[11] The correlation coefficients in Table 1 for these two systems show clearly that for chloromethylhomoarenes optimum correlation was obtained when a carbanion model was utilized. A radical anion model gave a superior correlation in the case of iodomethylhomoarenes. The dichotomy observed for the substituted benzyl halides is also present in these polycyclic compounds.

Nitrogen-containing heteroarylmethyl chlorides

Poor correlations were obtained when the logarithms of the relative rates of chlorine atom transfer from all isomeric chloromethylpyridines and chloromethylquinolines to triphenyltin radical were correlated with SCF–PPP[19,20]-calculated total energy differences.[13] The possible inadequacies of the SCF–PPP approach may be attributable to its failure to incorporate σ electron polarization as caused by the electronegative chlorine and nitrogen atoms present in the molecule. It was concern over this inadequacy that initiated the present work. AM1 is a semi-empirical all-valence-electron SCF method that takes into account electron polarization. The results of correlations of the logarithms of the relative rates for chlorine atom transfer versus AM1-calculated relative total energy differences are given in Table 1. The carbanion and radical anion models both yield improved correlations relative to those obtained by the SCF–PPP approach. It is the former model, however, which is superior. These results support the view that chlorine atom transfer from nitrogen heteroarylmethyl chlorides to triphenyltin radical involves a direct atom abstraction in the rate-determining step similar to that found in the previously discussed systems.

Oxygen-containing heteroarylmethyl chlorides

It was with some trepidation that the corresponding oxygen-containing heteroarylmethyl chlorides were treated. These systems (furans, benzofurans, dibenzofurans and dibenzo-*p*-dioxins) did not correlate well with SCF–PPP[19,20] calculations.[12] It is known that the AM1 calculation on furan is among the worst of all those reported by Dewar and co-workers.[16,17] The reason might be the poor choice of parameters for the oxygen atom present as part of an aromatic ring. In spite of the small reactivity range (*ca* 7·7) exhibited by this series of compounds, the correlations were not as poor as might have been expected. The correlation coefficients in Table 1 show again the carbanion to be a more suitable model. The most significant deviations from the correlation are exhibited by the smaller systems. If the cause of the poor fit is due to the parameters chosen for oxygen, the larger, benz-annelated heterocycles should show a better correlation as the weighted effect of the oxygen atom(s) becomes less. This was observed.

Alternative models for the electron-transfer mechanism

Further refinement of the electron-transfer model is possible. The calculations on the radical anion model were carried out with full geometric optimization. This corresponds to an adiabatic process which would physically allow for atomic reorganization prior to the carbon—halogen bond cleavage. An alternative is to assume that the electron transfer occurs by an isothermal process which does not allow for geometric reorganization.[22] In keeping with Koopman's theorem,[23] the relative LUMO energies were chosen to correlate the rate data of the systems investigated. The results are given in Table 1.

An examination of all the series of compounds considered shows an improvement over the radical anion model in only half of the cases. Although Moreno *et al.*[23] stated concern over the suitability of an approach using LUMO energy levels, it is of interest, however, that the two series of iodine-containing molecules both show improved correlations for the (E_{LUMO}) approach over the ($\Delta E_{\mathrm{T}}^{\mathrm{ra}}$) model.

Yet another alternative exists. Symons and Bowman,[24] in their work on the dehalogenation of chlorinated benzenes, argued that, in order to break the carbon—halogen bond in the radical anion, the electron has to be transferred from the Π system (presumably the LUMO) to the antibonding orbital of the bond to be cleaved. It might well be that the σ^* orbital plays the key role in the present system; a correlation with the relative energies of the carbon—chlorine antibonding molecular orbitals should be possible. In the case of the nitrogen-containing heteroarylmethyl chlorides, a correlation coefficient of 0·884 was obtained. This represents no substantial improvement over that found with the original radical anion model.

CONCLUSION

AM1 calculations represent an improvement over the SCF–PPP approach in modeling halogen atom transfer from benzylic substrates to organotin radicals. The results also support the view that there is an appreciable charge separation in the transition state of these reactions. If one considers the overall pictures, contrasting benzyl chlorides, chloromethylhomoarenes, nitrogen-heteroarylmethyl chlorides and oxygen-heteroarylmethyl chlorides with benzyl iodides and iodomethylhomoarenes, our findings support the dichotomy of mechanisms in that chlorine atoms are seemingly transferred by direct atom abstraction whereas iodine atom transfer proceeds via an electron-transfer mechanism. In view of recent work, we are tempted to include transfer of bromine in the first category, although our calculations do not provide a clear division between the two alternatives. Finally, the AM1 molecular orbital seems to be superior and more versatile than the SCF–PPP method in treating these systems.

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