

The Semiempirical Quantum Chemical Calculations of Different Parameters of Chosen Tin Hydrides

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ABSTRACT

The semiempirical quantum chemical method (MOPAC package) was applied to calculate the geometry, total energy and heats of formation of different tin hydrides to confirm that increased activity of the R_2SnXH type hydrides in the reaction of reduction of menthone is associated with their spontaneous decomposition.

Keywords: hydrostannation, MOPAC package

Diorganotin dihydrides, R_2SnX_2 , readily undergo disproportion on mixing with dialkyltin (IV) compounds R_2SnX_2 ($X =$ halide, carboxylate, sulphonate, etc.) to give, in equilibrium, new hydrides R_2SnXH , with different properties from these of the parent dihydrides or of more familiar trialkyltin hydrides, R_3SnH /1,2/. In particular, these new hydrides decompose at room temperature by a radical chain mechanism /3/, to give dihydrogen and corresponding tetraorganodistannane, XR_2SNSNR_2X /2,4/. By addition of a suitable substrate, the intermediate stannyl radicals can be diverted into hydrostannation or hydrostannolysis /3/. Davies /5/ has shown that these reactions with the reagents R_2SnXH exhibit different rates, and different chemo-, regio-, and stereo-selectivities from those involving trialkyltin hydrides. It has been explained by differences in the mechanisms of their initiations. In the case of Bu_2SnH_2 and Bu_3SnH , the hydrostannolysis of organic halides and the hydrostannation of alkynes and carbonyl compounds usually need elevated temperatures and the addition of a radical initiator; the hydrides R_2SnXH will bring about similar reactions in the absence of an added initiator.

In order to explain this effect, we have carried out theoretical calculations of chosen parameters for different tin hydrides. We have applied semiempirical PM3 quantum chemical calculations by means of the MOPAC 6.0 package /6,7/ for the purpose of calculating heats of formation of chosen tin hydrides.

In the PM3 method /8/, the appropriate one-centre-two-electron integrals, taken as the parameters of the method, were optimised. In the previous versions of MOPAC, using the MNDO and AMI (Austin Model 1) Hamiltonians /9/, were parameterised by means of experimental data for isolated atoms and were not optimised. It has been shown by Stewart /7/, for some hundred compounds, that such parameterisation

considerably improves, in comparison with AM1 and particularly with MNDO, the correlation with experimental values of such important calculated parameters as: the enthalpy of formation (ΔH_f), the dipole moment (μ), the ionisation energy (E_i), the bond lengths (r), and the planar and dihedral angles. The values of heats of formation were collected in Table I.

The MOPAC approach to the optimisation of the molecular geometry uses the derivatives of the energy with respect to the coordinates and changes the bond length and the planar and dihedral angle so as to lower the enthalpy of formation. When no further change can significantly lower the enthalpy of formation, the optimisation is stopped and the geometry of molecules then corresponds to a stationary point on the potential surface [7].

Table I

The heats of formation, ΔH_f , of different tin hydrides and corresponding stannyl radicals.

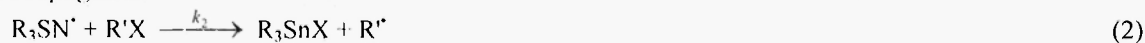
Compound	Heats of formation ($-\Delta H_f$)
	[kcal/mole]
1. Bu_3SnH	- 43.539
2. $\text{Bu}_3\text{Sn}^\cdot$	- 34.490
3. Bu_2SnH_2	- 15.931
4. $\text{Bu}_2\text{Sn}^\cdot\text{H}$	- 5.819
5. Bu_2SnHCl	- 52.817
6. $\text{Bu}_2\text{Sn}^\cdot\text{Cl}$	- 48.596
7. $\text{Bu}_2\text{SnH}(\text{OCOCH}_3)$	- 121.137
8. $\text{Bu}_2\text{Sn}^\cdot(\text{OCOCH}_3)$	- 118.965

The elementary steps in homolytic hydrostannolysis and homolytic hydrostannation are shown in eqns. (1) - (6) [5].

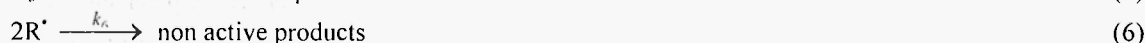
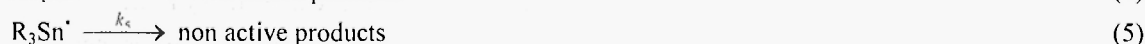
(i) *Initiation*



(ii) *Propagation*



(iii) *Termination*

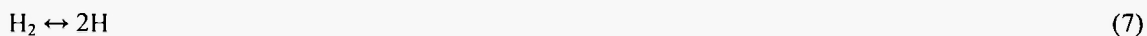


The overall rate of reaction will depend on the rates of these individual steps.

Therefore, it appeared to us that the spontaneity of the initiation step (1) for different tin hydrides should be a measure of their reactivity.

Values of heats of formation (ΔH_f) for different tin hydrides and corresponding stannyl free radicals are given in Table 1.

The literature value /10/ of the enthalpy of reaction of dissociation of hydrogen molecule



is equal to -104.167 kcal/mole.

Thus, the enthalpy of formation for the hydrogen atom may be assumed to be equal to 52.083 kcal/mole. The enthalpies of the reactions for the initiation step (1) for studied tin hydrides have been calculated as the following difference:

$$[\Delta H_f(\text{R}_3\text{Sn}') + \Delta H_f(\text{H})] - \Delta H_f(\text{R}_3\text{SnH})$$

and they have been collected in Table 2.

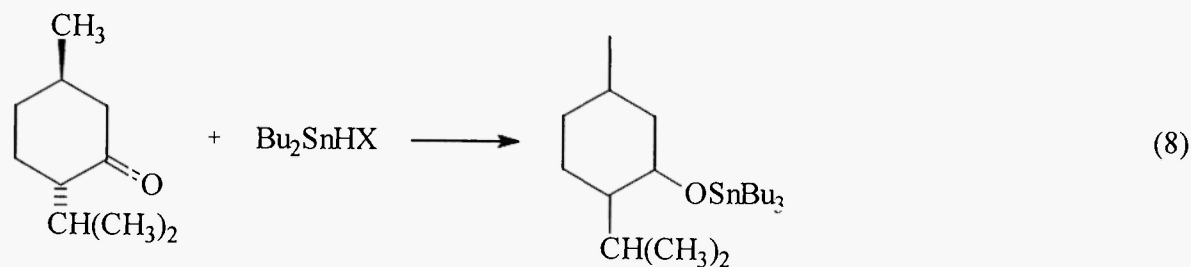
Table 2
The enthalpy of the initiation reaction for different tin hydrides

Compound	Enthalpy of the reaction [kcal/mole]
Bu ₃ SnH	61.132
Bu ₂ SnH ₂	62.195
Bu ₂ SnHCl	56.304
Bu ₂ SnH(OCOCH ₃)	54.255

The initiation step turns out to be an endothermic reaction for all studied hydrides.

However, for the last two mixed hydrides (Bu₂SnHX) considerably smaller values of the enthalpy of the reaction have been obtained.

The abovementioned results are in agreement with the experimental data of the reductions of (-)-menthone we carried out (9). We found that no reaction occurs between tributyltin hydride (1) and dibutyltin dihydride and (3), but the hydrides (5 and 7) react in 24 hours to give the tin derivative of menthol (eqn.8), and the sequence of reactivity correlates with changes of studied theoretical parameters reflecting the rate of homolytic decomposition at room temperature. It seems likely that the principal initiation involves spontaneous decomposition of the hydride and does not involve the carbonyl compound.



The purification of (10) by column chromatography leads to menthol.

Table 3

Percentage yields in the hydrostannation of menthone after 24 hours

Bu ₂ SnH ₂	Bu ₂ SnHCl	Bu ₂ SnH(OCOCH ₃)
0%	60%	80%

EXPERIMENTAL SECTION

Dibutyltin dihydride was prepared by treatment of dibutyltin dichloride with lithium aluminium hydride in over 50% excess as described by van der Kerk /11/. Subsequent ether extraction and distillation gave the required dihydride in quantitative yield.

Dibutyltin chloride hydride was prepared by a disproportionation reaction between dihydride and dibutyltin dichloride /1,12,13/, whereas acetoxydibutyltin hydride was prepared by the analogous disproportionation reaction between the dihydride and diacetoxydibutyltin /1,12,13/. Tributyltin hydride was a commercial sample. A typical example of reduction was as follows: (3) dibutyltin dihydride 117.7 mg (0.5 mmole) and diacetoxydibutyltin 175.5 mg (0.5 mmol) were added to 2 cm³ of benzene. After 10 minutes, when equilibrium was reached, 154.2 mg (1.0 mmol) of (-)-menthone were added. The progress of reaction was monitored by TLC and ¹H NMR spectroscopy. After 24 hours, the product of the reaction was purified by a column chromatography using a mixture of ethyl acetate and petroleum ether (2/8 v/v) as eluent. The product was identified as menthol by comparison of its ¹H NMR spectrum with the literature data /14/.

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