

PHYSICAL VERSUS CHEMICAL QUENCHING OF ELECTRONICALLY EXCITED BENZENE BY Me_3SnH

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Summary

Theory and e.p.r. experiments show that upon electronic excitation, benzene loses its D_{6h} symmetry; the description of the $^1B_{2u}$ state by a 1,3-diradical (with zwitterionic character) and that of the $^3B_{1u}$ state by a 1,4- or a 1,2-diradical has been proposed and found viable. However, it would be interesting to know whether these diradicals can be considered as such with respect to the chemical reactivity of the states. The chemical quenching of excited benzene by Me_3SnH , a species highly reactive towards free radicals, has thus been attempted. We obtained no evidence for any reaction of the triplet benzene whilst the singlet did react but only scarcely; instead the tin hydride acted as a moderate intersystem crossing catalyst as evidenced by the fluorescence quenching and by the enhanced Φ_p/Φ_f ratio observed for benzene. The decay to the ground state in fluid solutions ultimately involves a step of energy transfer to the hydride which partly decomposes. Similar results were obtained for the intramolecular quenching studied on β -phenethylidimethyltin hydride.

Introduction

According to Bryce-Smith and Longuet-Higgins [1] and to Bryce-Smith [2] one can rationalize and justify the photochemical behaviour of benzene on the basis of a 1,3-diradical (with more or less zwitterionic character [3]) arising from the $^1B_{2u}$ state and of 1,2- or 1,4-diradicals tautomeric with the $^3B_{1u}$ state. Although there is experimental evidence [4] that the D_{6h} symmetry is lost upon excitation (at least for the $^3B_{1u}$) it is, however, not clearly established at present [5] whether these radicals should be taken for more than canonical representations and in particular whether they display to a significant extent the chemical properties of radicals as does, for instance, the triplet carbonyl group [6].

In view of the ambiguous nature of the distorted (relaxed) excited states of benzene it appeared that Me_3SnH , which is known to be highly reactive towards free radicals [7], would be a best suited quencher in the

sense that it should be efficient either in chemically reacting with a molecule exhibiting free radical character (as do *e.g.* S_1 conjugated dienes [8], carbonyls [7a, b], some polycyclic aromatic triplets [9] etc.) or in catalyzing intersystem crossing by heavy atom effect, as was recognized for Me_4Sn [10], if the excited state is chemically inert. We have thus investigated the fate of the excited phenyl chromophore under the influence, either inter- or intramolecular, of a Sn-H group, using a mixture of benzene with trimethyltin hydride in one case and β -phenethyl dimethyltin hydride as the substrate in the other.

Experimental

Reagents

Me_3SnH was synthesized according to the procedure of Akhtar and Clark [11], distilled at atmospheric pressure under helium and stored under helium at $-20^\circ C$; it presents an end band absorption in the u.v., with $\epsilon_{254} = 0.086$.

β -Phenethyl dimethyltin hydride ($\phi-CH_2-CH_2-SnMe_2H$) has been prepared by reducing the corresponding bromide* with $LiAlH_4$ as described by Van Der Kerk [12], distilled under reduced pressure (b.p. $65^\circ C/3$ Torr) and stored under helium at $-20^\circ C$; it was characterized by i.r., mass, n.m.r. and u.v. spectroscopies; the u.v. spectrum is almost superimposable to that of ethylbenzene with $\epsilon_{260}^{max} = 232$ and $\epsilon_{254} = 196$.

Cyclohexane for u.v. spectroscopy, from Fluka, was redistilled before use.

Methylcyclohexane (purum from Fluka) and 3-methylpentane (purum from Aldrich) were percolated through activated silica in order to remove any phosphorescent impurities and proved transparent in the u.v. down to 220 nm.

Spectroscopic Uvasol benzene from Merck was used as such.

Photolyses and product identification

All photolyses were performed in sealed cells on carefully degassed clear solutions; this was particularly critical since tin hydrides are highly reactive towards oxygen and then produce a turbid solution due to the insoluble alkyltin oxides.

Mixtures of benzene with Me_3SnH (1:1 to 3:1 by vol.; benzene absorbs all the light in these conditions) were irradiated in n.m.r. tubes at room temperature by the main output (253.7 nm) of two low pressure mercury arcs and excitation in the vapour phase was avoided by wrapping an aluminium foil from below the liquid level; a constant geometry set up allowed the experimental conditions to be reproduced accurately. The light intensity as measured by the benzophenone sensitized isomerization of 1,3-pentadienes was 7.5×10^{15} quanta $s^{-1} ml^{-1}$.

* The bromide was obtained by a general synthetic method [13].

The reaction progress was followed by n.m.r. spectroscopy and the photolysis was extended as long as the product formation remained linear with time. Quantitative measurements were rendered difficult by the slow deposit of tin (a neutral filter) on the walls but this effect was minimized by frequently shaking the cell which resulted in removal of the deposit and gathering of metal particles in the bottom of the tube. At the end of a run the photolyzate was checked by u.v. to ensure that benzene had remained the only light absorbing species and was thereafter quantitatively analyzed by vapour phase chromatography (v.p.c.) on a SE 52 column; the products were trapped at 77 K for spectroscopic identification. Metallic tin was determined by weighing. Besides light hydrocarbons which were not analyzed (presumably methane and ethane based on the v.p.c. retention time), two products were formed, the first of which was readily identified as $\text{Me}_3\text{Sn-SnMe}_3$ on the basis of its mass and n.m.r. spectra; the second had a molecular weight of 246 (for isotope ^{120}Sn), it had n.m.r. absorptions at δ 5.7 (2H,m), 2 - 1.2 (7H,complex) and 0.2 (9H,s) and its i.r. spectrum was identical to that reported by Kuivila [14] for 4-cyclohexenyltrimethyltin which thus fits all of the data.

β -Phenethyldimethyltin hydride was photolyzed in 1 M cyclohexane solution as described above; the reaction was followed by n.m.r. but it was not possible to achieve reasonably accurate quantitative measurements, owing to the formation of a red polymer of the type $\text{R}(\text{R}_2\text{Sn})_n\text{R}$ which contributes to the absorption of light. The crude photolyzate was analyzed by v.p.c. and there was a detectable amount of light hydrocarbons and one major product identified as ethylbenzene by comparison with an authentic sample.

Irradiation of neat Me_3SnH has been performed at 253.7 nm in a 1 cm pathlength cell ($OD = 0.75$) and the hydride decomposition proceeded with a low quantum efficiency of $\sim 10^{-3}$ as determined by weighing metallic tin at the end of a run; besides methane and ethane the v.p.c. analysis revealed only trace amounts of $\text{Me}_3\text{Sn-SnMe}_3$ and Me_4Sn as the sole products.

Quantum yields were not determined in the vapour phase photolysis but it was readily estimated, at the vapour pressure above the liquid, that for both direct excitation and energy transfer from benzene the deposit of tin on the walls was at least 10 to 100 times faster than in solution.

Luminescence measurements

Quenching of benzene fluorescence

The fluorescence of benzene was measured at 22 °C in outgassed cyclohexane at constant optical density of 0.5 and increasing concentrations of Me_3SnH (0 to 0.5 M; in these conditions the contribution of the hydride to light absorption is negligible); the spectra were recorded on a home-made fluorimeter equipped with a Bausch & Lomb monochromator (1350 grooves per mm grating, blazed at 300 nm; synchronous motor drive scanning), a RCA/1P28/VI photomultiplier, a 427 current amplifier from Keithley (gain

10^{11} V/A) and a Hewlett-Packard 7004B X-Y recorder. The light source was a low pressure Rayonet RPR Hg arc from which the 253.7 nm line was selected for excitation.

Phosphorescence to fluorescence ratios

Outgassed glassy solutions of β -phenethyldimethyltin hydride or of benzene/ Me_3SnH mixtures in 3-methylpentane/methylcyclohexane (1:3 by vol) were excited at 253.7 nm at 77 K in cylindrical tubes, using the typical quartz Dewar devised by Aminco. The values of Φ_P/Φ_F were derived from the integrated intensity of the emission bands; the correction for photomultiplier response (in terms of quantum efficiency) is negligible in the range of wavelength used.

Results and Discussion

An extended irradiation of benzene dissolved in Me_3SnH resulted essentially in the decomposition of the hydride with production of metallic tin and light hydrocarbons, together with the formation of hexamethylditin and 4-cyclohexenyltrimethyltin; the quantum yields are equally low for all three products: $\Phi(\text{Sn}) \sim 5 \times 10^{-4}$; $\Phi(\text{Me}_6\text{Sn}_2) \sim 2 \times 10^{-4}$; $\Phi(\text{C}_6\text{H}_8\text{SnMe}_3) \sim 2 \times 10^{-4}$. The production of metallic tin indicates that benzene transfers energy to the hydride and it was thus necessary to determine the efficiency of direct photodecomposition of Me_3SnH ; when neat Me_3SnH is photolyzed alone it gives rise to trace amounts of $\text{Me}_3\text{Sn-SnMe}_3$ and Me_4Sn and to light hydrocarbons and metallic tin with an approximate quantum yield of not more than 10^{-3} , *i.e.* similar to the figure obtained by energy transfer. This means that a large part of the energy absorbed by benzene is ultimately distributed to the tin hydride but brings no information as to the mechanism of transfer and wastage; this point will be discussed later on in connection with fluorescence and phosphorescence measurements.

The formation of Me_6Sn_2 and of 4-cyclohexenyltrimethyltin as the sole adduct, in the ratio 1 : 1, is readily accommodated by the following scheme:

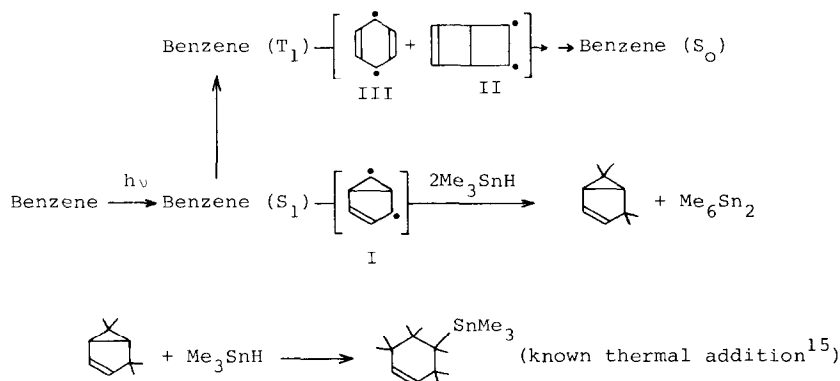


TABLE 1

Fluorescence quenching of benzene by Me_3SnH in cyclohexane at 20 °C

$[\text{Me}_3\text{SnH}]$ (mol/l)	0.05	0.11	0.19	0.25	0.32	0.41	0.54
F^0/F	1.04	1.14	1.21	1.33	1.40	1.48	1.69

and suggests that only the singlet excited state is reduced by the quencher. However, the reaction takes place with such a low quantum yield that one could hardly consider the tautomer (I) as a real diradical (or zwitterion) *chemically* distinct from the initially populated $^1\text{B}_{2u}$ state; the same applies to the triplet state where II and III should have led to 1,3- and 1,4-cyclohexadienes or to the corresponding tin-containing adducts. But prior to reaching this definite conclusion and since energy transfer was seen to occur, it was necessary to ensure that the $^1\text{B}_{2u}$ and/or the $^3\text{B}_{1u}$ states did not directly collapse into the $^1\text{A}_{1g}$ state while interacting with the tin hydride. We found that the fluorescence of benzene in cyclohexane is indeed quenched by Me_3SnH (see Table 1), obeying the usual Stern–Volmer relationship $(F^0/F) - 1 = k_q\tau_{S_1} [\text{Me}_3\text{SnH}]$ where $k_q\tau_{S_1} = 1.24$ l/mol; taking [16] $\tau_{S_1} = 2.9 \times 10^{-8}$ s it follows that $k_q = 4.3 \times 10^7$ $\text{l mol}^{-1}\text{s}^{-1}$ which compares with 6×10^9 $\text{l mol}^{-1}\text{s}^{-1}$ for the diffusion rate constant in cyclohexane at 20 °C.

The important point here is that Me_3SnH is just as poor a quencher as Me_4Sn [10]; therefore the failure of S_1 benzene to react with the hydride actually reflects a chemical inertness which contrasts with the high quantum yields reported for several concerted cycloadditions to olefins [17]. Besides we have determined the phosphorescence to fluorescence ratio of benzene at 77 K in the presence of increasing amounts of Me_3SnH (see Table 2) and it clearly follows that the tin derivative acts as an intersystem crossing catalyst; this is evidence that the $^3\text{B}_{1u}$ state neither sensitizes nor reacts with the quencher to an appreciable extent. Hence in order to justify the energy transfer from benzene to Me_3SnH in fluid solution, we are left with the explanation that *subsequent* to the catalyzed intersystem crossing of the triplet benzene moiety involved in an encounter complex, trimethyltin hydride picks up vibrational energy and dissociates in its ground state, to the small extent of its low decomposition quantum yield, prior to Boltzmann equilibration with the surroundings just as it likely does when directly ex-

TABLE 2

 Φ_P/Φ_F for benzene as a function of $[\text{Me}_3\text{SnH}]$; measured at 77 K on 3-methylpentane/methylcyclohexane glassy solutions

$[\text{Me}_3\text{SnH}]$ (mol/l)	0	0.67	1.25	1.75
Φ_P/Φ_F	0.53	0.73	1.11	1.20

cited by light. That the hydride dissociation occurs in a "hot" ground state is further supported by the fact that it proceeds much faster in the vapour than in the condensed phase as well by energy transfer from benzene as by direct irradiation.

The influence of an intramolecular perturbation of the phenyl chromophore, such as that which may obtain in β -phenethyltrimethyltin hydride, led to very much the same results. Thus under irradiation at 253.7 nm a fluid solution of this compound in cyclohexane developed a deep red colour which is assigned [18] to polymeric Sn^{II} materials* and indicates that here too the energy initially absorbed by the benzene moiety eventually ends up to a detectable extent in Sn-H and Sn-C vibrational modes. The v.p.c. analysis of the photolyzate shows no evidence for any chemical quenching of the phenyl group; the only products which were retrieved, apart from the non-volatile red polymers, were light hydrocarbons and ethylbenzene, the later being formed with a low quantum yield roughly estimated to $\lesssim 10^{-2}$. Again the tin atom catalyzes the $T_1 \rightarrow S_0$ transition as evidenced by the value of Φ_P/Φ_F which raises from 0.94 for toluene [5] to 5.75 in this case and by the spectacular enhancement of the forbidden O-O emission; the heavy atom effect is too weak however for observing the $T_1 \leftarrow S_0$ absorption (see Fig. 1). The $T_1 \rightarrow S_0$ catalysis (enhanced phosphorescence) due to the tin atom and the low efficiency for ethylbenzene formation in fluid solution (22 °C) are consistent with the concept of vibrational energy being partitioned in the ground state molecule and reinforce the conclusion at which we arrived in discussing the intermolecular case; indeed besides the possibility for directly abstracting a hydrogen atom from the Sn-H moiety (*i.e.* reduction of the phenyl group), a radical-like substituent on tin would have assisted effectively the homolytic cleavage** of the weak Sn-H bond with subsequent production of dimethyltin and ethylbenzene. Therefore there is no indication whatsoever that S_1 or T_1 benzene should be regarded as diradical entities as far as their chemical behaviour is concerned.

Conclusion

Although calculations and e.p.r. measurements lead to particular diradical (or zwitterionic) descriptions which distinguish between the $^1B_{2u}$ and the $^3B_{1u}$ states of benzene, it appears that this kind of representation is oversimplified and unadapted from the standpoint of chemical reactivity. The occurrence of 1,4- addition arising exclusively from the triplet state of benzene has indeed been recently questioned [17, 20] and in view of the

* This contrasts with the intermolecular quenching and might be due to the partition of energy among more numerous vibrational modes; photodecomposition of Et_4Sn *e.g.*, also yields a red polymer [18].

** Such a mechanism is exemplified by the carbonyl $\pi^* \leftarrow n$ excitation of 3-oxobutyl-trimethyltin which results primarily in the homolytic cleavage of the oxobutyl-Sn bond [19].

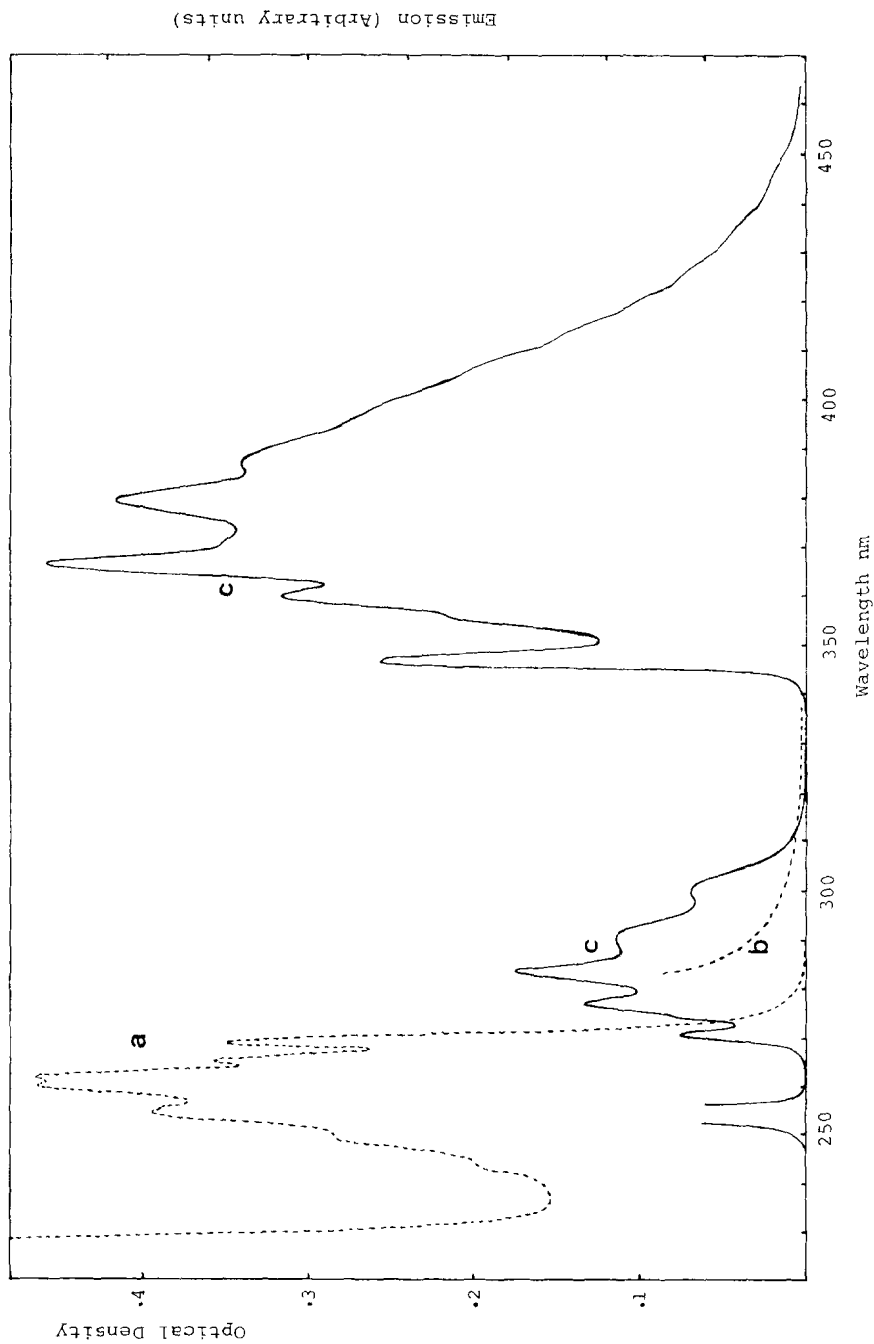


Fig. 1. Spectroscopic characteristics of β -phenethylidimethyltin hydride. (a) Absorption of a 2×10^{-3} mol/l solution in cyclohexane; (b) *ibid.*, 10^{-1} mol/l solution; (c) fluorescence and phosphorescence emission from a 2×10^{-3} mol/l solution in 3-methylpentane/methylcyclohexane, at 77 K.

present results it seems likely that the amplitude of electron localization in these diradicals (distorted states) is so weak that other factors might well overwhelm its effects.

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