

"SPIN-CHARGE EXCHANGE" IN A STABLE RADICAL-CARBANION, AND RELATED
 INTERMOLECULAR ONE-ELECTRON TRANSFERS

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ABSTRACT: An example of a rapid spin-charge exchange in a stable radical-carbanion, with independent radical and anion sites, is described. A related anionization of radicals with HO^- is also reported and interpreted.

By treatment with an alkaline hydroxide in DMSO, perchlorotriphenylmethyl radical (PTM \cdot) -a paradigm of an inert free radical¹- is converted quantitatively into perchlorotriphenylmethylcarbanion (PTM $^-$).^{2,3} We have recently found that this can most conveniently be accomplished with tetrabutylammonium hydroxide in THF. Such a puzzling one-electron transfer is tentatively explained through the formation of a transient p- π charge-transfer complex between hydroxide ion and radical PTM \cdot (HO-PTM^-) (Figure 1) which is assisted by the powerful, cumulative electron-withdrawing effect of the numerous ring chlorines. Such a radical-anion complex would react somehow as a hydroxyl radical, leaving carbanion PTM $^-$ behind.

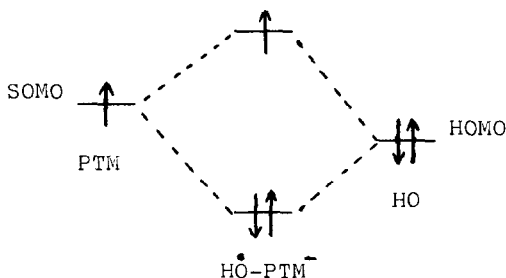
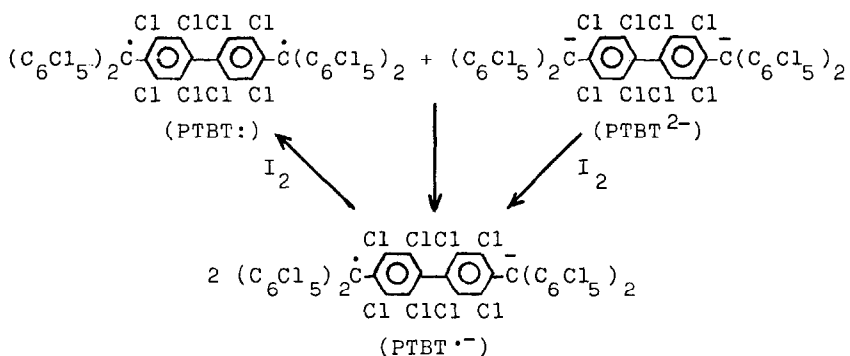


Figure 1. Frontier-orbital diagram for CT complex HO-PTM^-

Inert free diradical perchloro- $\alpha, \alpha', \alpha', \alpha'$ -tetraphenylbi-*p*-tolyl- α, α' -diyl (PTBT:) reacts also with $\text{Bu}_4\text{N}^+\text{HO}^-$, in THF, to give perchloro- $\alpha, \alpha', \alpha', \alpha'$ -tetraphenylbi-*p*-tolyl- α, α' -diyl dianion (PTBT²⁻) in an excellent yield. A mixture of equimolecular amounts of diradical PTBT: and PTBT²⁻ in THF, at room temperature, undergoes a rapid electron transfer yielding an equilibrium the major component of which is perchloro- $\alpha, \alpha', \alpha', \alpha'$ -tetraphenylbi-*p*-tolyl- α, α' -diyl radical anion (PTBT^{•-}), along with those initial components. This equilibrium can also be attained by controlled oxidation of dicarbanion PTBT²⁻ with iodine.



In this connection it is pointed out that the biphenyls show an intense UV-Visible "biphenyl" (conjugation) band due to delocalization of their π -electrons in both rings. Whenever a biphenyl possesses relatively bulky substituents in all their four central ortho positions then no vestige of the "biphenyl" band is observed, a fact due to complete steric inhibition of resonance or delocalization.⁴ This evanescence has also been described for numerous chlorine-substituted biphenyls and the locations of the remaining spectral maxima are practically coincident with those of closely-related benzene analogues.^{5,6} This phenomenon is due to the perpendicularity between the two benzene rings of the biphenyl system which is caused by the strong repulsions among those ortho substituents, as corroborated in decachlorobiphenyl by the X-ray diffraction data (angle of $\sim 87^\circ$);⁷ therefore the π molecular orbitals of its two moieties are orthogonal.

For the same token, the UV-Visible spectra of diradical PTBT: and dianion PTBT²⁻ (wavelengths and absorptivities) are coincident with those of monoradical PTM[•] and monoanion PTM⁻, respectively,¹ which is inconceivable

if there were in those species any "biphenyl" absorption left. Furthermore, the UV-Visible absorption curve (two bands) of the equilibrium mixture of PTBT:, PTBT²⁻, and PTBT^{•-} -where the latter predominates greatly, as shown by ESR (see later)- is exactly the superposition (average) of the PTBT: and PTBT²⁻ curves (one band each) (Figure 2). Such wave-length and absorptivity coincidence, and the absorption additivity demonstrate that the PTBT^{•-} molecular moieties are electronically independent and, consequently, no biphenyl odd-electron delocalization takes place.

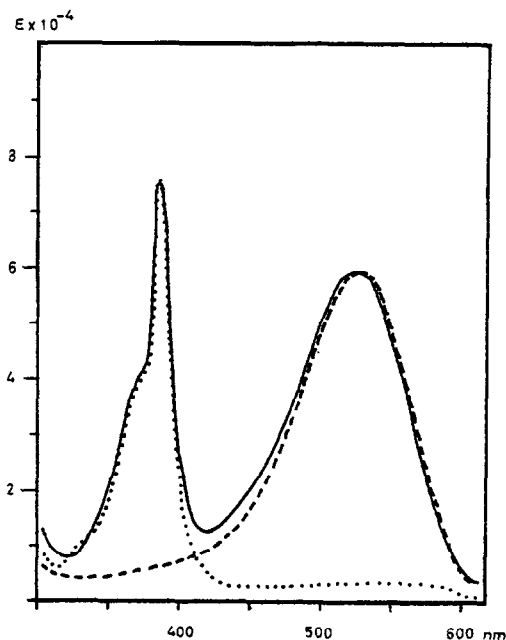
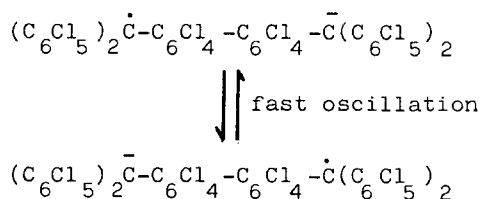


Figure 2

UV-visible spectra (THF)

- PTBT:;
- PTBT²⁻;
- equilibrium mixture where PTBT^{•-}/PTBT: > 8

The ESR spectrum of radical-carbanion PTBT^{•-} shows alpha (41.5 MHz) and ortho (15.0) ¹³C spin couplings half as high those for diradical PTBT: (82.5 and 30.0 MHz) (or radical PTM), as if -within the ESR time scale- the spin densities at those carbon nuclei were also half as high. Since lone-electron delocalization is ruled out, those abnormal hyperfine couplings indicate that PTBT^{•-} is subjected to a fast "spin-charge exchange". In other words, the molecule of PTBT^{•-} possesses a full negative charge localized in one moiety and a full odd electron in the other moiety, as shown by its UV-Visible spectrum. Its negative charge and odd electron exchange positions rapidly, and consequently, the ESR technique "sees" only the average electronic structure; i.e., half negative charge and half odd electron in each PTBT^{•-} moiety, as it has been observed in a related radical-carbenium ion.⁶



The recorded ESR data cannot be accounted for by assuming a fast intermolecular electron transfer for, under the conditions of the measurements, mixtures in THF of closely related radical PTM[•] and carbanion PTM⁻, display normal ¹³C couplings.

The mixture of carbanions PTBT²⁻ and PTBT^{•-}, in equilibrium with PTBT:, has been analyzed through acid quenching. Also, the PTBT^{•-}/PTBT: concentration ratio has been obtained from the relative intensities of the ¹³C ESR lines.

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