mass spectrum, *m/e*: 160 (M^+, **4a**), 140 (M^+ - HF, **4a**), 112 (M^+ - HF - CO, **4a**), 101 (M^+ - CH_2COOH, **4a**), 73 (M^+ - CH_2COOH - CO, **4a**). HRMS (*m/e*) for $C_6H_5FO_4$: Calcd 160.0172, found 160.0173.

Product Mixture from Isomerization of *cis,cis*-3-Fluoromuconate (1a) in DCl. ^{1}H NMR (D_2O, 200 MHz): δ 8.24 (d, **2a**, *J* = 5.7 Hz), 7.59 (d, **4a**, *J* = 5.7 Hz), 7.51 (d, **2b**, *J* = 5.7 Hz), 6.51 (d, **2a**, *J* = 5.7 Hz), 6.48 (d, **2b**, *J* = 5.7 Hz), 6.35 (d, **4a**, *J* = 5.7 Hz), 5.92 (s, **2a**), 5.61 (s, **2b**), 3.2 (m, **4a**). Integration of the ^{1}H NMR spectrum gave a ratio of **2a**/**2b**/**4a** of 40%/11%/49%.

Product Mixture from Isomerization of *cis,cis*-3-Chloromuconate (1b) in HCl. ^{1}H NMR (methanol-d_4, 200 MHz): δ 8.59 (dd, **3b**, *J* = 0.6 Hz, *J* = 15.4 Hz), 6.49 (dd, **3b**, *J* = 0.6 Hz, *J* = 15.4 Hz), 6.39 (t, **3b**, *J* = 0.6 Hz), 6.36 (d, **5b**, *J* = 1.8 Hz), 5.44 (m, **5b**), 3.08 (dd, **5b**, *J* = 3.5 Hz, *J* = 16.8 Hz), 2.66 (dd, **5b**, *J* = 16.8 Hz, *J* = 7.9 Hz). Integration of the ^{1}H NMR spectrum gave a ratio of **5b**/**3b** of 88%/12%. Integration of the ^{1}H NMR spectrum of the reaction run in DCl showed only deuterium incorporation into the C-5 position of **5b**. EI mass spectrum of 3-chloromuconolactone (**5b**), *m/e*: 178 (M + 2), 176 (M^+), 160 (M + 2 - H_2O), 158 (M^+ - H_2O), 140 (M^+ - Cl), 132 (M + 2 - HCOOH), 130 (M^+ - HCOOH), 119 (M + 2 - CH_2COOH), 117 (M^+ - CH_2COOH). HRMS (*m/e*) of 3-chloromuconolactone (**5b**) ($C_6H_5ClO_4$): calcd 175.9876, found 175.9877.

Product Mixture from Isomerization of *cis,cis*-3-Bromomuconate (1c) in HCl. ^{1}H NMR (methanol-d_4, 200 MHz): δ 8.51 (dd, **3c**, *J* = 15.1 Hz, *J* = 0.9 Hz), 6.65 (dd, **3c**, *J* = 0.7 Hz, *J* = 0.9 H), 6.52 (d, **5c**, *J* = 1.8 Hz), 6.44 (dd, **3c**, *J* = 15.1 Hz, *J* = 0.7 Hz), 5.46 (m, **5c**), 3.09 (dd, **5c**, *J* = 16.8 Hz, *J* = 3.6 Hz), 2.63 (dd, **5c**, *J* = 16.8 Hz, *J* = 7.9 Hz). Integration of the ^{1}H NMR spectrum gave a ratio of **5c**/**3c** of 92%/2%. Integration of the ^{1}H NMR spectrum of the reaction run in DCl showed only deuterium incorporation into the C-5 position of **5c**. EI mass spectrum of 3-bromomuconolactone (**5c**), *m/e*: 204 (M + 2 - H_2O), 202 (M^+ - H_2O), 177 (M + 2 - COOH), 176 (M + 2 - HCOOH), 175 (M^+ - COOH), 174 (M^+ - HCOOH), 163 (M + 2 - CH_2COOH), 161 (M^+ - CH_2COOH), 141 (M^+ - Br). HRMS (*m/e*) of 3-bromomuconolactone (**5c**) ($C_5H_4BrO_2$ (M^+ - COOH)), calcd 174.9395, found 174.9396.

Stability of 4-Fluoromuconolactone (4a) at pH 7.0. A sample of 4-fluoromuconolactone (**4a**) (2 mg) was dissolved in the pH buffer (100 mM KD_2PO_4, D_2O, pH 7.0, 1 mL) in an NMR tube. The mixture was monitored by ^{1}H NMR for 4 h. No change in the initial spectrum was observed. ^{1}H NMR (pH buffer, 200 MHz): δ 7.87 (d, 1 h, *J* = 5.7 Hz), 6.58 (d, 1 h, *J* = 5.7 Hz), 3.30 (m, 1 h), 3.16 (m, 1 h).

Isomerization of *cis,cis*-3-Fluoromuconate (1a) in Concentrated H_2SO_4. *cis,cis*-3-Fluoromuconate (**1a**) (30 mg) was dissolved in concentrated H_2SO_4 (5 mL) and the resultant mixture stirred at room temperature for 1 h. An equal volume of ice water was added, and the mixture was extracted with ether. Evaporation of the organic phase yielded the product mixture, which was analyzed by ^{1}H NMR. ^{1}H NMR (D_2O, 200 MHz): δ 8.24 (d, **2a**, *J* = 5.7 Hz), 7.51 (d, **2b**, *J* = 5.7 Hz), 6.51 (d, **2a**, *J* = 5.7 Hz), 6.48 (d, **2b**, *J* = 5.7 Hz), 5.92 (s, **2a**), 5.61 (s, **2b**). Integration of the ^{1}H NMR spectrum gave a ratio of **2a**/**2b** of 56%/44%. Isomerization of **1a** in concentrated D_2SO_4 was carried out as described for concentrated H_2SO_4. The chemical shift values of the resonances of **2a** and **2b** were identical (Figure 5). Integration of the ^{1}H NMR spectrum gave a ratio of **2a**/**2b** of 58%/42%. The resonance corresponding to H_5 in **2a** and **2b** showed 50% deuterium incorporation.

Acknowledgment. We thank the National Institutes of Health (Grant GM 37210) for support of this research.

Unique Single-Electron Transfers between Chemically Inert Triphenylmethyl Radicals and Triphenylmethyl Anions

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A number of SET reactions between inert 4-X-tetradecachlorotriphenylmethyl radicals (X-PTM•) and stable tetra-*n*-butylammonium (Q^+) 4-Y-tetradecachlorotriphenylmethides (Q^+ Y-PTM:$^-$; X, Y ≡ H, Me, NH_2CO, Me_2NCO, Ph_2NCO, MeOCO, PhOCO, NH_2, MeO, Cl, Br, $^-$OCO) have been studied in THF, at room temperature, by the ESR technique. These processes are abnormally slow, since no significant ESR linewidth and/or hyperfine coupling changes are observed. In the SET between H-PTM• and NH_2-PTM:$^-$ the progress has been monitored by ESR, and its second-order rate constant is 5×10^2 mol^{-1} L min^{-1}. Such a unique, most remarkable slowness is ascribed to colossal steric hindrance (shielding) caused by chlorine overcrowding in both SET components. The SET equilibrium constants K_{ET} have been calculated from the ESR spectrum, using radicals H-PTM• and Me-PTM• as the standards, and they follow the Hammett equation. Exceptions are X = MeO or RCO, due to steric inhibition of resonance. Evidence indicates that the SET process occurs between the radical and the free carbanion, in spite the latter existing predominantly as an ion pair with counterion Q^+, as shown by osmometry. The syntheses and isolation in excellent yields of a substantial number of new inert free radicals and new related stable carbanion salts have been effected, most of the latter from the corresponding radicals, using hydroxide ion as a single-electron donor.

Single-electron transfer (SET) is a fundamental process in chemistry. Although many organic reactions involve it, on account of the high reactivity and instability of the free-radical species involved as starting components, intermediates, or final products, those that allow a deep insight and a straightforward, unambiguous interpretation of the relevant phenomena are rather scarce.

An outstanding SET class occurs among carbanions, carbenium ions, and trivalent carbon free radicals. Unfortunately, research work on it is dramatically lacking because of the unavailability of both ionic and radical species provided with sufficient stability and low reactivity in non-SET processes. Spectral evidence for a reversible SET between 4,4′-bis(dimethylamino)triphenylcarbenium ion and 4,4′,4″-trinitrotriphenylcarbanion, giving their free radicals, has been reported.[1] The reaction of equivalent amounts of perchlorotriphenylmethyl cation, $(C_6Cl_5)_3C^+$,

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[1] Arnett, E. M.; Molter, K. E.; Marchot, E. C.; Donovan, W. H.; Smith, P. *J. Am. Chem. Soc.* **1987**, *109*, 3788.

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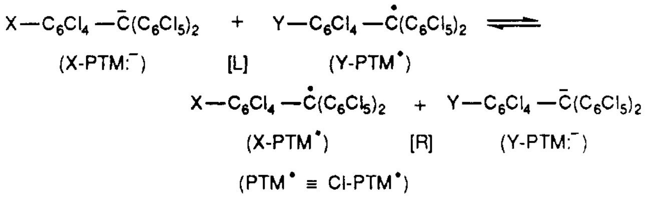
Scheme I



$$\underset{(X\text{-PTM}:^-)}{X{-}C_6Cl_4{-}\bar{C}(C_6Cl_5)_2} \underset{[L]}{+} \underset{(Y\text{-PTM}^\bullet)}{Y{-}C_6Cl_4{-}\dot{C}(C_6Cl_5)_2} \rightleftharpoons \underset{(X\text{-PTM}^\bullet)}{X{-}C_6Cl_4{-}\dot{C}(C_6Cl_5)_2} \underset{[R]}{+} \underset{(Y\text{-PTM}:^-)}{Y{-}C_6Cl_4{-}\bar{C}(C_6Cl_5)_2}$$

$(PTM^\bullet \equiv Cl\text{-}PTM^\bullet)$

and perchlorotriphenylmethyl anion, $(C_6Cl_5)_3C:^-$, affords almost quantitative yields of perchlorotriphenylmethyl radical (PTM•).[2] Related covalent-bond-forming coupling between 4,4′,4″-trianisylmethyl cation and (nitrophenyl)malononitrile anion has been published.[3] SET rates between tris(*p*-nitrophenyl)methyl radical and its carbanion,[4] and between triphenylmethyl,[5] 9-phenylacridinyl, and *N*-methyl-9-phenylacridinyl radicals[6] and their respective cations, have been estimated from ESR line broadening.

The exceptional inertness of the IFRs,[7] such as perchlorotriphenylmethyl radical (PTM•), as well as the high stability and low reactivity of their carbanions,[8,9] derive mainly from their molecular steric shielding by their numerous chlorine substituents which preserve the carbon skeleton, especially the radical and carbanion reaction sites, i.e., those possessing the highest electron spin and negative charge densities, respectively.

$$\underset{(PTM^\bullet)}{(C_6Cl_5)_3C^\bullet} \qquad \underset{(PTM:^-)}{(C_6Cl_5)_3C:^-}$$

However, in spite of their colossal chemical inertness, the IFRs are active in certain one-electron oxidations and reductions, such as the reaction of PTM• with $SbCl_5$ giving the corresponding carbenium ion PTM$^+$,[7e,10,11] and its reaction with ascorbic acid, giving carbanion PTM:$^-$.[7e,12]

$$\underset{(PTM:^-)}{(C_6Cl_5)_3C:^-} \xleftarrow{+e} \underset{(PTM^\bullet)}{(C_6Cl_5)_3C^\bullet} \xrightarrow{-e} \underset{(PTM^+)}{(C_6Cl_5)_3C^+}$$

This remarkable behavior is attributed to the genuine electron transfers being rather insensitive to steric shielding. The SET-donor and the SET-acceptor species are assumed not to require approach to distances where steric repulsions are forbidding, as in bond-forming reactions.

It was decided to investigate possible SET processes between IFRs of the PTM• class, substituted in one para position, and their noncorresponding carbanions, and eventually to ascertain the relevant substituent effects (Scheme I).

As starting components, the following IFRs and tetra-*n*-butylammonium carbanion salts [R_4N^+ X-PTM:$^-$] have been synthesized and isolated in pure, solid state.

(a) Salts $(n\text{-}C_4H_9)_4N^+\ X\text{-}C_6Cl_4\text{-}\bar{C}(C_6Cl_5)_2 \equiv Q^+\ X\text{-PTM}:^-$

X ≡ H,[13] Me,[13] NH_2CO,[13] Me_2NCO,[13] Ph_2NCO,[13] MeOCO,[13] PhOCO,[13] NH_2,[13] MeO,[13] Cl,[13] Br,[13] ^-OCO.[13]

(b) Radicals $X\text{-}C_6Cl_4\text{-}\dot{C}(C_6Cl_5)_2 \equiv X\text{-PTM}^\bullet$

X ≡ H,[14] Me,[14] NH_2CO,[15] Me_2NCO,[13] Ph_2NCO,[13] MeOCO,[14] PhOCO,[13] NH_2,[11] MeO,[11] Cl,[7b] Br.[14]

The SETs here investigated involve either *pH*-tetradecachlorotriphenylmethyl or *p*-methyltetradecachlorotriphenylmethyl (S-PTM•/S-PTM:$^-$; Y ≡ S ≡ H, Me) pairs as *reference compounds*.

Four general methods have been used to synthesize the radicals.

(a) From *αH*-triphenylmethanes:

$$X\text{-}C_6Cl_4\text{-}CH(C_6Cl_5)_2 \xrightarrow{HO^-} X\text{-}C_6Cl_4\text{-}\bar{C}(C_6Cl_5)_2 \xrightarrow{-e} X\text{-PTM}^\bullet$$

X ≡ H, Me, Cl

$$HO_2C\text{-}C_6Cl_4\text{-}CH(C_6Cl_5)_2 \xrightarrow{HO^-} {}^-OCO\text{-}C_6Cl_4\text{-}\bar{C}(C_6Cl_5)_2 \xrightarrow[(-CO_2)]{Br_2} Br\text{-PTM}^\bullet$$

(b) From other radicals:

$$HO\text{-PTM}^\bullet \xrightarrow{CH_2N_2} MeO\text{-PTM}^\bullet$$

$$ClCO\text{-PTM}^\bullet \xrightarrow{ZH} ZCO\text{-PTM}^\bullet$$

(Z ≡ NH_2, PhO, Ph_2N, Me_2N)

X ≡ MeO, NH_2CO, PhOCO, Ph_2NCO, Me_2NCO

(c) From a carbanion salt:

$$MeOCO\text{-}C_6Cl_4\text{-}\bar{C}(C_6Cl_5)_2 \xrightarrow{I_2} MeOCO\text{-PTM}^\bullet$$

(d) From a fuchsonimine:

$$NH{=}C_6Cl_4{=}C(C_6Cl_5)_2 \xrightarrow{Sn^{2+}} NH_2\text{-PTM}^\bullet$$

The radicals synthesized here for the first time have been characterized by elemental analysis and ESR, UV–vis, and IR spectra. The state of purity of those already described has been verified likewise.

Synthesis of the carbanion tetra-*n*-butylammonium salts:

(a) From αH compounds:

$Q^+ \equiv n\text{-}Bu_4N^+$

$$X\text{-}C_6Cl_4\text{-}CH(C_6Cl_5)_2 \xrightarrow{HO^-} Q^+\ X\text{-PTM}:^-$$

X ≡ H, Me, Cl, MeOCO, ^-OCO

(b) From the corresponding radicals:

$$X\text{-PTM}^\bullet \xrightarrow{HO^-} Q^+\ X\text{-PTM}:^-$$

X ≡ H, Me, Cl, MeO, NH_2, Br, NH_2CO, Me_2NCO, Ph_2NCO, PhOCO

This reduction is carried out in THF with $n\text{-}Bu_4N^+$ HO^-. It is pointed out that the first reduction of IFRs with HO^- as a SET donor was reported by Ballester et al.[7a,16] as early

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Table I. ESR Experimental Data for Radicals X-PTM$^\bullet$

X	solvent	*g*	line width G	line width % G[a]	α-, bh-,[b] *o*-^{13}C couplings, G
$^-$OCO	THF	–	1.2	30	–
NH_2[11]	C_2Cl_4	2.0027	0.93		27.9, 11.1, 9.8
	THF		2.09	0	
Me[14]	C_2Cl_4	2.0027	1.25		29.6, 10.4
	THF		1.35	100	
MeO[11]	C_2Cl_4	2.0027	1.35		29.5, 12.5, 10.7
	THF		1.1	60	
H[14]	C_2Cl_4	2.0027	1.25		29.7, 12.6, 10.2
	THF		1.22	68	
NH_2CO[15]	C_2Cl_4	2.0023	1.45		30.1, 12.9, 10.7
	THF		1.22	50	
Ph_2NCO	C_2Cl_4	2.0022	0.9	60	30.4, 13.2, 10.7
	THF		1.2	50	
MeOCO[14]	CCl_4	2.0024	1.57		29.5, 12.4, 10.4
	THF		1.27	50	
Me_2NCO	C_2Cl_4	2.0022	0.95	70	30.6, 13.2, 10.2
	THF		1.12	75	
Cl[7b]	C_2Cl_4	2.0026	1.43		29.5, 12.5, 10.7
	THF		1.32	48	
Br[14]	CCl_4	2.0033	1.71		29.2, 12.5, 9
	THF		1.5	35	
PhOCO	C_2Cl_4	2.0023	0.97	70	30.6, 13.2, 10.5
	THF		1.2	0	

[a] Gaussian contribution to line width. [b] bh ≡ bridgehead.

as 1967 and investigated and employed by them thereafter.[7d,e,9]

The tetra-*n*-butylammonium salts have been characterized, and their purity checked, by elemental analysis and UV–vis and IR spectra. The yields of procedures a and b are excellent. These salts, except Q$^+$ NH_2-PTM:$^-$ and Q$^+$ Me-PTM:$^-$, are most stable in air and in homogeneous aqueous solution. It appears that NH_2-PTM:$^-$ and Me-PTM:$^-$ salts in solution are sensitive to O_2, the former giving radical NH_2-PTM$^\bullet$ slowly, and the latter decomposing to another carbanion.

The SETs between the radicals and the carbanions have been monitored by ESR spectrometry. Small changes in the ESR parameters (*g* values, coupling constants, linewidth, and Gauss–Lorentz hybridization) are observed. In Table I the ESR spectral parameters for radicals here employed are given.

As expected, in spite of the extreme overcrowding by chlorines of both radical and carbanion, under the reaction conditions the SETs between carbanions X-PTM:$^-$ (or S-PTM:$^-$) and radicals S-PTM$^\bullet$ (or X-PTM$^\bullet$) do take place. In all but two cases the process virtually stops well before 10 min have elapsed, the radical ratio [X-PTM$^\bullet$]/[S-PTM$^\bullet$] remaining practically constant thereafter. Therefore, the SETs are too fast to be followed kinetically by straightforward observation of the ESR spectrum.

With Standard H-PTM. The SETs with H-PTM reference have been studied starting both by oxidation of X-PTM:$^-$ (dyad L) and by reduction of X-PTM$^\bullet$ (dyad R), i.e., in both directions for the equation in Scheme I (Figure 1, top). The Guldberg–Waage mass–action law is closely followed, as disclosed by the runs where the radical/carbanion ratios vary from 1 to 5 or 10 (Table V, supplementary material). Except in the SETs involving the NH_2-PTM system, to be considered later, the equilibrium constants K_{ET} calculated from L and from R (Table II) are virtually coincident, since in both equilibrium is nearly reached.[17]

Table II

$$\underset{[L]}{Q^+\ X\text{-}PTM^- + S\text{-}PTM^\bullet} = \underset{[R]}{X\text{-}PTM^\bullet + Q^+\ S\text{-}PTM^-}\ (Q^+ \equiv n\text{-}Bu_4N^+)$$

equilibrium constant

$$K_{ET} = [X\text{-}PTM^\bullet][Q^+\ S\text{-}PTM^-]/[S\text{-}PTM^\bullet][Q^+\ X\text{-}PTM^-]$$

and free energy change ΔG_{ET}, from data of Table V, supplementary material

system X/S	K_{ET} L	K_{ET} R	K_{ET} mean	ΔG_{ET}, kcal mol^{-1}
S ≡ H				
$^-$OCO/H[a]	–	–	–	–
NH_2/H	–	–	32.7[b]	2.03
CH_3/H	–	5.00	5.00	0.94
MeO/H	3.27 3.28	3.90 3.45	3.56	0.74
H/H	–	–	(1.000)	(0.00)
NH_2CO/H	0.363	0.475	0.416	–0.51
Ph_2NCO/H	0.250	0.397	0.315	–0.67
MeOCO/H	0.278	0.231	0.253	–0.80
Me_2NCO/H	0.176	0.178	0.177	–1.01
Cl/H	0.130	0.189	0.157	–1.08
Br/H	0.137	0.099	0.117	–1.25
PhOCO/H	0.052	0.036	0.043	–1.83

S ≡ Me	K'_{ET} L	K'_{ET} R	K_{ET}[d]
MeO/Me	0.620	–	3.10
NH_2CO/Me	0.064	–	0.320
Ph_2NCO/Me	0.050	–	0.250
H/Me	0.200	–	1.000
Me_2NCO/Me	0.031	–	0.155
PhOCO/Me	0.010	–	0.050
MeO/Cl[c]	7.4	7.3	

[a] Also, when the molar ratio is 2:1, an equimolecular mixture of $^-$OCO-PTM$^\bullet$ and H-PTM$^\bullet$ results. [b] Extrapolated value (see the Hammett equation). [c] About 15 times higher concentrations. Semimicroorganic analysis. [d] Obtained by multiplying K'_{ET} by 5.000.

The equilibrium data described above have been confirmed by carrying out, for some SET systems, three tetradic SET reactions, i.e., starting from an equimolecular mixture of the four components (two radicals, two car-

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[17] Because of slower, minor side-reactions, reaction times over three hours have generally been waived.

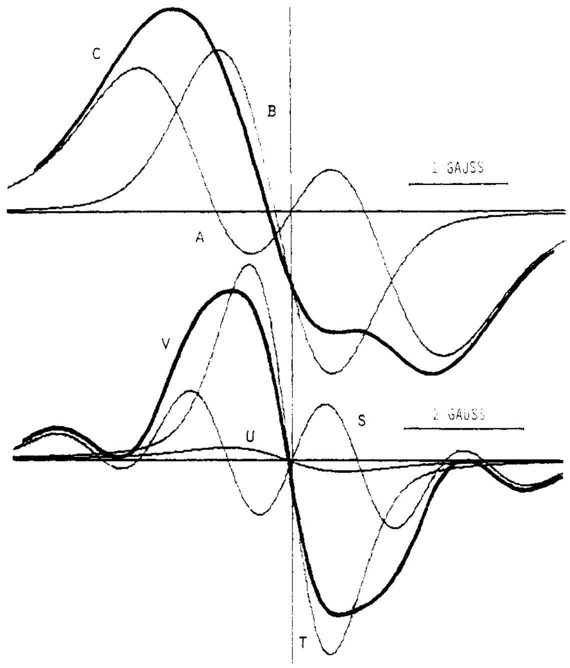

Figure 1. Analysis of radical mixtures by ESR computer simulation. Top: A, H-PTM•; B, Me_2NCO-PTM•; C, H-PTM• (0.71) + Me_2NCO-PTM• (0.29). Bottom: S, Me-PTM•; T, MeO-PTM•; U, $HOCH_2$-PTM•; V, Me-PTM• (0.50) + MeO-PTM• (0.44) + $HOCH_2$-PTM• (0.06).

banion salts). Such reactions were carried out by mixing in THF, under the usual conditions, equal volumes of (a) two solutions of same concentrations, resulting from the 1:1 SETs S-PTM•/Q^+ X-PTM:$^-$, and X-PTM•/Q^+ S-PTM:$^-$; (b) two solutions, same concentrations, of equimolecular amounts of S-PTM• *plus* Q^+ S-PTM:$^-$, and X-PTM• *plus* Q^+ X-PTM:$^-$; (c) two solutions, same concentrations, of equimolecular mixtures of S-PTM• *plus* X-PTM•, and Q^+ S-PTM:$^-$ *plus* Q^+ X-PTM:$^-$. The end points of the three tetrads, found by computer simulation, coincide practically.

Computer simulation data for the system H-PTM:$^-$/NH_2-PTM• shows that, even using a large excess of H-PTM:$^-$, the ratios remain near their initial values, i.e., little reaction occurs. However, the reverse NH_2-PTM:$^-$/H-PTM• exchange does take place, being slow enough to be followed (up to 1 h) by a direct ESR technique (see later). These results indicate that the SET equilibrium is much shifted to the right-hand side of the equation in Scheme I, and the L and R exchanges take place very slowly.

With Standard Me-PTM. The same procedure as with standard H-PTM has been used (Figure 1, bottom). Nevertheless, as mentioned before (see Syntheses of the Carbanion Salts), $(n\text{-}Bu)_4N^+$ Me-PTM:$^-$ is unstable. When decomposition is allowed to proceed under the SET reaction conditions (3.5 h), at higher concentration (6×10^{-3} mol L^{-1}), about 50% of the carbanion is converted into at least one other carbanion salt. The latter has been made to react with iodine, giving a third inert free radical T. From the ESR, IR spectrum, and chromatographic behavior it is concluded it is the known $HOCH_2$-PTM•.[18] In this connection it is emphasized that while the ESR spectrum of Me-PTM• consists of four well-resolved main lines (spin coupling with the three protons),[14] the radicals RCH_2-PTM• (R ≠ H) type display one line, instead the expected three lines (coupling with two protons).[18] Nevertheless, their linewidth is unusually high (1.9 vs ≈1.3 G), suggesting the presence of unresolved proton couplings.[19] This is caused by two high energy barriers, due to steric repulsions with the two ortho chlorines, in the rotation of the RCH_2^- around its bond axis with the para carbon.[19]

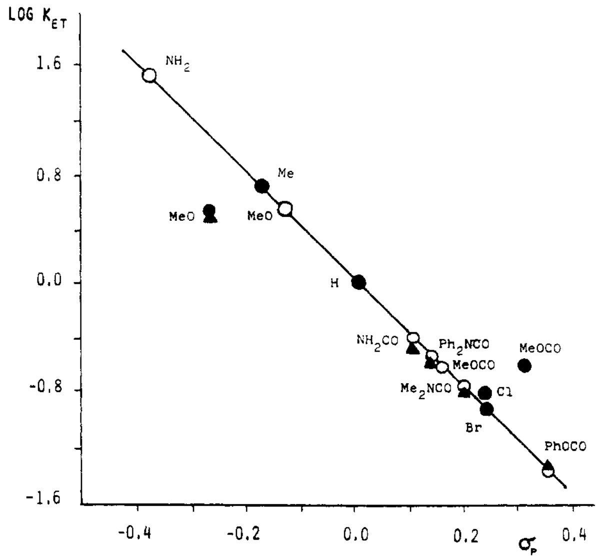

Figure 2. Hammett K_{ET}/σ_P plot. (●), from literature; (○), calculated using standard H-PTM (L + R); (▲), using standard Me-PTM (L).

Therefore, the SET series using the system Me-PTM as standard suffers to a variable extent from partial decomposition of the reference system to give $HOCH_2$-PTM•. While *for oxidation of X-PTM:$^-$ (L) the perturbation due to $HOCH_2$-PTM• is almost insignificant* (Table II), in the reverse reaction R is vast (15–40% of radical T), including the spectrum of radical T in the computer simulation. This, which causes the noncoincidence of the two dyad end points, evidences that the decomposition of Me-PTM:$^-$ takes place initially at a rate close to that of the SET process.

Consequently, the X-PTM/Me-PTM series have been calculated exclusively from dyads L, and the reported data include an approximate correction for a minor proportion of radical T and its carbanion, the latter in equilibrium with the main SET components (Table II). The SET involving the NH_2-PTM pair has not been studied. Nevertheless, some experiments indicate that both L and R SETs are, as with standard H-PTM, very slow. (Systems Cl/Me, Br/Me, and MeOCO/Me have not been studied either.)

In order to improve accuracy, the *adopted* K_{ET} value has been calculated by averaging log K_{ET} for L and R K_{ET}s and taking the antilogarithm of the mean value obtained. The K_{ET}s, including Me-PTM as the standard, are shown in Table II, as well as the free energy changes ΔG.

The order of decreasing substituent effect (K_{ET} values) is: $^-OCO > H_2$[20] > Me > MeO > H > NH_2CO > Ph_2NCO > MeOCO > Me_2NCO > Cl > Br > PhOCO.

Data from the sequence using the H-PTM standard system has been adopted to test fit to the Hammett equation. Figure 2 represents the Hammett plot, i.e., log K_{ET} vs the generally accepted substituent σ_P values.[21-23]

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(18) Ballester, M.; Veciana, J.; Riera, J.; Castañer, J.; Rovira, C.; Armet, O. *J. Org. Chem.* **1986**, *51*, 2472.

(19) It arises from the mutual cancellation of the methylene bonding and anti-bonding hyperconjugation with the benzene electronic π-system. This is caused by the steric repulsions between R and the two ortho chlorines which force and keep the two methylene hydrogens on the same side of the benzene ring.

(20) By extrapolation.

Table III. Hammett Correlation Data

substituent	K_{ET} L	K_{ET} R	K_{ET} adopted	log K_{ET}	σ_p
NH_2	–	–	32.7[a]	1.51	–0.38[b]
Me	–	5.00	5.00	0.700	–0.170[b] –0.172
MeO	3.27	3.90	3.56	0.552	–0.268[b] –0.134
			(1.000)	(0.000)	(0.000)
NH_2CO	0.363	0.475	0.416	–0.381	0.103
Ph_2NCO	0.250	0.397	0.315	–0.501	0.134
MeOCO	0.278	0.231	0.253	–0.596	0.31[b] 0.158
Me_2NCO	0.176	0.178	0.177	–0.752	0.198
Cl	0.130	0.189	0.157	–0.804	0.227[b] 0.211
Br	0.137	0.100	0.117	–0.932	0.232[b] 0.244
PhOCO	0.052	0.036	0.043	–1.364	0.354

substituent (dyad L)	K'_{ET}	K_{ET}[c]	log K_{ET}	σ_p
MeO	0.620	3.10	0.49	–0.268[b]
Me	(1.000)	5.00	0.70	–0.170[b]
H	0.200	1.00	0.00	0.000[b]
NH_2CO	0.064	0.320	–0.49	0.103[d]
Ph_2NCO	0.050	0.250	–0.60	0.134[d]
Me_2NCO	0.031	0.155	–0.81	0.198[d]
PhOCO	0.010	0.050	–1.30	0.354[d]

[a] Extrapolated. [b] From literature.[21–23] [c] $K_{ET} = 5.000K'_{ET}$. [d] Reported here.

the σ_P values for Br, Cl, H, Me (filled circles) follow closely the Hammett equation, and they have been used to define the linear regression. The reason for exclusion of substituents of RCO type and MeO, which render useless their reported σ_P values, is given below. The linear regression gives log $K_{ET} = -3.91\sigma_P$. Its correlation coefficient is 0.9981, and, therefore, according to Jaffé's yardstick,[24] it is excellent. From this linear regression, the σ_P values for substituents PhOCO, Me_2NCO, MeOCO, Ph_2NCO, not recorded in the literature, have been calculated (Table III; Figure 2, open circles).

As indicated earlier, using the Me-PTM as the standard, dyads L are the only ones providing reliable data. Therefore, K'_{ET} recorded in Table III are *L* values, being close to those obtained from K_{ET}, as shown in the Hammett plot (Figure 2, filled triangles). However, the points fall somewhat below the regression line, and this is because they result from the L dyads only. In fact, when the linear regression is performed *taking the K_{ET} from approximate L Values only (Table II), the points turn out on the line.*

It is well known that substituents RCO and RO, which are provided with π- and p-electrons, interact strongly with the benzene π-electron system. In the species dealt with here, prohibitive steric repulsions between the flanking two ortho chlorines and the Z group of those substituents occur in the conformation where the former lies in the plane of the benzene ring, causing those substituents to rotate about their bond axis with the ring and so reduce π-electron resonance. Accordingly, the esters and amides here investigated are resonance-inhibited, and their substituent σ_P values, calculated with the expression here reported, should be much lower than in nonperchlorinated compounds. Thus, both the electron-attracting character of the carbonyl and the electron-donating character of the MeO are significantly diminished. In fact, taking their conventional σ_P values, the points representing the MeO-CO and the MeO substituents in the Hammett plot appear well *above* and *below* of the regression line respectively (Figure 2), as expected. This effect must also be true for the substituent PhOCO and the amides.

The slope of the Hammett plot or reaction constant ρ, a measure of the susceptibility of a reaction to the substituent effect, is negative (–3.91), meaning that the more electron-attracting the substituent X, the lower the proportion of radical X-PTM$^\bullet$ at equilibrium. The electron-donating substituents favor the transfer of a single electron from carbanion X-PTM:$^-$, and the electron-attracting substituents in the radicals, by raising their electron affinity, favor the formation of the carbanions.

The highest calculated σ_P value is not that of Br, as might be expected, but that of PhOCO (Table III). This is attributed to the electron-attracting character of phenyl. Notice also that the SET from dianion $^-$OCO-PTM:$^-$ to H-PTM$^\bullet$ is practically complete, evidencing the dramatic enhancement of the SET donor character due to the additional negative charge of the substituent. The log K_{ET} of the amino group has been extrapolated using its σ_P value and the linear regression expression.

That type of steric inhibition of resonance involving RCO and RO substituents on these perchlorinated rings has already been established by UV–vis spectral studies.[25–28] The *substituent (spectral) transition moment*, which correlates with the molar absorptivity of the ^1L_b (secondary) benzenoid band,[27–29] is much sensitive to resonance inhibition effects, since it depends almost exclusively upon the conjugation. This has been studied in anisole and resonance-inhibited 2,6-dimethylanisole,[28] the MeO transition moment in the latter being much smaller.

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(29) Ballester, M.; Riera, J. *Tetrahedron* **1964**, *20*, 2217.

Table IV. Mean Molecular Weight (MMW) of Tetr-*n*-butylammonium Carbanion Salts, Radicals, and Carbanion Salt/Radical, 1:1, Binary Mixtures by Osmometry in THF, at 45 °C

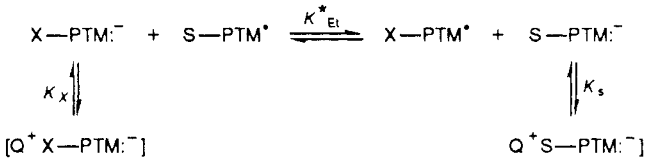
		mean molecular weight		
system	Dyad	calcd	obsd	dif, %
(a) Radical and Radical Mixtures				
H-PTM$^\bullet$		725	698	−4
Cl-PTM$^\bullet$		760	790	4
Me-PTM$^\bullet$/PhOCO-PTM$^\bullet$		792	898	13
Cl-PTM$^\bullet$/H-PTM$^\bullet$		743	765	3
(b) Salts and Salt Mixtures				
NH$_2$-PTM$^-$		983	1040	6
Me-PTM$^-$		982	1013	3
H-PTM$^-$		968	878	−9
Cl-PTM$^-$		1002	964	−4
PhOCO-PTM$^-$		1088	1163	7
Me-PTM$^-$/H-PTM$^-$		975	1099	13
Ph$_2$NCO-PTM$^-$/H-PTM$^-$		1065	1058	−1
PhOCO-PTM$^-$/Me-PTM$^-$		1035	1042	1
H-PTM$^-$/Cl-PTM$^-$		985	966	−2
(c) Radical and Corresponding Carbanion Salts				
NH$_2$-PTM$^\bullet$/NH$_2$-PTM$^-$		862	935	8
MeO-PTM$^\bullet$/MeO-PTM$^-$		877	955	9
Me-PTM$^\bullet$/Me-PTM$^-$		861	914	6
H-PTM$^\bullet$/H-PTM^{-a}		847	976	15
Cl-PTM$^\bullet$/Cl-PTM$^-$		881	860	−2
PhOCO-PTM$^\bullet$/PhOCO-PTM$^-$		967	945	−2
(d) Radical and Noncorresponding Carbanion Salts				
NH$_2$/H	L	854	904	6
	R	854	957	12
MeO/H	L	862	870	1
	R^a	862	1055	22
Me/H	L^a	854	1035	21
	R^a	854	1256	47
Ph$_2$NCO/H	L^a	944	1131	20
	R^a	944	1303	38
Cl/H	L	864	866	0
	R	864	912	5
PhOCO/H	L	907	954	5
	R	907	968	7
NH$_2$/Me	L	861	949	10
	R	861	969	12
MeO/Me	L	869	866	0
	R	869	851	−2
Ph$_2$NCO/Me	L	951	914	−4
	R	951	1013	6
PhOCO/Me	L^a	914	1429	56
	R^a	914	1117	22

[a] Conclusive evidence for complexes.

Since the Me group is homomorphic with Cl,[30,31] the steric inhibition of MeO-PTM should likewise reduce the σ_P value, as found.

Concerning the system NH$_2$-PTM/H-PTM, both NH$_2$-PTM$^\bullet$ and NH$_2$-PTM:$^-$ appear to be much resonance stabilized, as indicated by simple molecular orbital considerations, more so the former than the latter. In fact, while other perchlorinated free radicals display in the UV–vis absorption spectrum two main "radical bands", with maxima near 385 and 500–560 nm (red radicals),[7] those of the NH$_2$-PTM$^\bullet$ radical are bathochromically shifted to 390 and 553–598 nm (green radical),[11] suggesting that resonance in the radical is quite significant. Similarly, the "carbanion band", found normally around 515 nm[9] in NH$_2$-PTM:$^-$, appears bathochromically shifted to 772 nm. Therefore, resonance stabilization is the decisive factor in the equilibrium unbalance observed in NH$_2$-PTM/H-PTM SET system.

Scheme II



$K_X = [Q^+][X\text{-PTM:}^-]/[Q^+\ X\text{-PTM:}^-]$
$K_S = [Q^+][S\text{-PTM:}^-]/[Q^+\ S\text{-PTM:}^-]$
$K^*_{ET} = [X\text{-PTM}^\bullet][S\text{-PTM:}^-]/[S\text{-PTM}^\bullet][X\text{-PTM:}^-]$

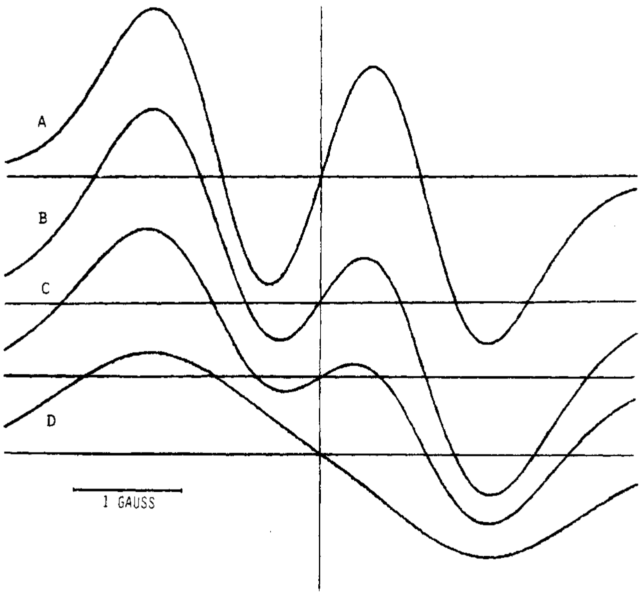


Figure 3. Progress of the SET between NH$_2$-PTM:$^-$ and H-PTM$^\bullet$ (1:1) monitored by ESR spectrum. A, 0 min, spectrum of H-PTM$^\bullet$; B, 20 min; C, 40 min; D, spectrum of pure NH$_2$-PTM$^\bullet$.

Mean molecular weight (MMW) determinations show (Table IV, column 4) that in THF, at concentrations 40-fold higher than that of the SETs, *the carbanion and its counterion are present as ion pairs*, at least overwhelmingly. Nevertheless, a low concentration of free ions is not ruled out.

In SET processes, ion pairs react much slower than the free ions.[32,33] If an ion pair/free carbanion equilibrium exists, resulting in a minor proportion of carbanion, and the electron transfer occurs, mostly at least, between radical and free carbanion, the experimental X-PTM$^\bullet$/S-PTM$^\bullet$ ratio should be sensitive to large concentration variations (Scheme II), provided the two ion pair dissociation equilibrium constants involved differ much.

However, some limitations imposed by the ESR spectrometer prevented the authors from performing these measurements at much higher concentrations. Therefore, it was decided to investigate the MeO-PTM/Cl-PTM SET systems on a semipreparative scale ($\approx 3 \times 10^{-3}$ mol L^{-1}; a 15-fold higher concentration) since the σ_P of substituents MeO and Cl differ much (Table III; Figure 2); and consequently the relevant ion-pair dissociation constants. The L and R SETs give practically the same equilibrium composition, the MeO-PTM$^\bullet$/Cl-PTM$^\bullet$ experimental ratio being $\approx$7.5 (reproduced) (Table II). From the K_{ET}s of

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systems MeO-PTM/H-PTM and Cl-PTM/H-PTM, measured at ESR concentrations, the K_{ET} for MeO-PTM/Cl-PTM is calculated, being ≈25. Such a vast K_{ET} difference indicates the existence of ion-pair dissociation equilibria.

Since the σ_P value (Figure 3) of H is much closer to that of CH_3O, the corresponding relevant K_x and K_s should not differ much, and consequently the K_{ET} values of system MeO-PTM/H-PTM performed at high and at low concentration should not differ much either. Accordingly, it has been found that the K_{ET} values (reproduced) are practically coincident (Table II). It is concluded therefore that *the free carbanions are either the sole or the main reacting species.*

Those results and conclusions have a significant bearing as far as the Hammett equation, since the experimental equilibrium constant is

$$K_{ET} = [\text{X-PTM}^\bullet][\text{Q}^+\ \text{S-PTM:}^-]/[\text{S-PTM}^\bullet][\text{Q}^+\ \text{X-PTM:}^-]$$

while the real SET constant is K^*_{ET}. Therefore $K_{ET} = K^*_{ET}K_x/K_s$. If $K_x \approx K_s$, then K_{ET} K^*_{ET}.

Because of steric shielding of the perchlorinated carbanions and the overcrowding of the tetra-*n*-butylammonium cation about their respective charge centers (the negative methyl carbon and the positive nitrogen), it is reasonable that the ammonium counterion moves close to the vicinity of a less shielded para position of the carbanion. This should be accompanied by a simultaneous partial migration of the carbanion negative charge from the highly shielded α-carbon to that para position by a resonance mechanism. In perchloro-organic chemistry, the tendency of the counterion to migrate to a distal position has been made evident, for example, in perchlorotriphenylcarbenium tetrachloroaluminate ($(C_6Cl_5)_3C^+\ AlCl_4^-$) (chlorine–*p*-carbon bridging with $AlCl_4^-$).[7c,34,35] In this connection it is mentioned that, from X-ray data on K (18-crown-6)$^+$ Cl-PTM:$^-$,[36] the minimal distances between its potassium and carbon atoms are those with para (4.3 Å) and meta (4.2 Å) carbons (distance with the α-carbon: 7.9 Å).

No significant changes (line broadening, hyperfine coupling constant halving) of the ESR spectrum, traceable to a very rapid spin exchange, are here observed, showing that the SET processes here reported are *unusually slow*, compared with electron exchange in conventional systems, and in allodial[7e] radical carbanions.[9,37] As will be seen next, this is made quite evident in the system NH_2-PTM:$^-$/H-PTM$^\bullet$.

It is reasonable that in the perchlorinated species here studied the "contact" distance between the radicaloid and the carbanionoid portions constituting the transition state, be abnormally long because of their steric shielding (overcrowding) by the chlorine substituents. For most spheroidal molecules, the estimated radius in SET processes is about 5 Å,[32] i.e., 10 Å between geometrical centers of the reacting molecules, approximately. This value should presumably be increased in the species dealt with here by at least twice the van der Waals chlorine radius (3.2 Å). On account of that greater separation, the transition-state energy should be *significantly higher* than that involved in smaller, nonsterically shielded (conventional) reacting species. Such a transition-state destabilization accounts for the observed exceptional slowness of the SETs between the free carbanions and the radicals.

In this connection it must be emphasized that, as shown by others,[32,33,38] ion pairs react much slower than the free ions. In addition, the ion pairs are here highly shielded and therefore reluctant to undergo intermolecular reactions, a familiar phenomenon in perchloroorganic chemistry.[7e] Steric hindrance and reorganization energy in the counterion transfer from the ensuing ion pair to the resulting ion pair are probably contributing factors to slowness as well. Therefore, most likely, *the ion pairs do not contribute significantly to the SET reaction rates.*

In the unique case of the SETs involving NH_2-PTM$^\bullet$ where, as already indicated, both the radical and the carbanion are largely stabilized by resonance, the transition-state energy must be significantly higher than that of the rest of X-PTM systems. Consequently, the rates of *both* the L and R SETs should be even much slower. Since the value of the equilibrium constant of that system, estimated from the Hammett plot (Figure 2), shows that the equilibrium lies much on R side, an approximate calculation of the NH_2-PTM:$^-$/H-PTM$^\bullet$ (L side) second-order rate constant from the kinetic data is allowed (Figure 3). Its value at room temperature is $k_{ET} \approx 5 \times 10^2$ mol^{-1} L min^{-1}.

In conclusion, regardless of the species involved, free carbanions and/or ion pairs, *the SET processes appear to be sensitive to steric hindrance.*

The osmometric data of Table IV indicate that in certain systems, at concentrations about 40-times higher than those normally employed (2×10^{-4} mol L^{-1}), complexes are present. Within the maximum experimental error (about 10%), it appears that they do not occur between radicals or between carbanion salts (Table IV, sections a and b). There is no indication either that complexes occur between radicals and their corresponding salts (Table IV, section c). However, at the end-point mixture of some SETs (Table IV, section d; marked), the difference between the observed MMW and its theoretical value for the ion pair is substantial and positive in sign. Therefore, *the formation of complexes may be significant only when a carbanion salt and a radical of dissimilar substitution are involved.*

It is remarkable that the proportion of complex resulting from dyad L is in some cases Table IV, section d) much different than that from dyad R. A clear-cut case is that of dyads MeOH, which display a most asymmetrical behavior, while in L there is no appreciable complex formation; in R the MMW difference is 22%, equivalent to 37% of complex. This lack of symmetry shows that either the SET and/or complex equilibria are not reached.

Such complexes are assumed to be, at least predominantly, of 1:1 type, those formed from the L and R components being [S-PTM$^\bullet$; Q$^+$ X-PTM:$^-$] and [X-PTM$^\bullet$; Q$^+$ S-PTM:$^-$], respectively. They are initially formed at a rate comparable to that of the relevant SET process. Once the complexes are formed, interconversion of them can only occur by dissociation, giving their original components, followed by SET. Since both the apparent (forward minus reverse) rate of the dissociation process, and the apparent rate of the SET should dramatically diminish at higher (40-fold) concentration, the latter because of increased

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association of the carbanions to non-SET reacting ion pairs, it is reasonable that, within the usual reaction times, complex equilibration may not take place. This conclusion should be valid for complexes of type higher than 1:1.

The fact that for significant complex formation two different substituents are required suggests they are of polar character. In this connection, it is pointed out that in systems X-PTM/H-PTM, where X is PhOCO or Cl, no complex is observed (Table IV). This indicates that in this case complex dissociation, giving free ion and radical, is assisted by those substituents, which are the two most electron-attracting ones dealt with here (Figure 2 and Table III).

Nevertheless, the structure of these complexes and the driving force leading to them remain obscure; the lack of pertinent evidence does not allow an entirely satisfactory rationalization. These are subjects deserving a detailed study, which the authors have not undertaken for they are well beyond the purpose and scope of the SET research program embraced here.

Experimental Section

General Methods and Equipment. The IR, UV–vis, and ESR spectra have been recorded with Perkin-Elmer Model 682, Perkin-Elmer Model Lambda Array 3840, and Varian Model E109 spectrometers, respectively. The osmometric measurements have been performed with a V.P. Knauer Model 73111 osmometer. For the ESR spectra simulations, an Olivetti M-24 computer has been employed using programs devised by the authors specifically, including Gauss–Lorentz hybrid line shapes.

In general, the pure radicals have been obtained after elimination of impurities by chromatography (silica gel or alumina), using CCl_4 or CCl_4/hexane.

The SETs have been carried out in air, in the dark. Osmometric measurements have been performed on some of the radicals and carbanion salts. The resulting mean molecular weights (MMW) are given in Table IV.

Since the IR spectra of perchloroorganic compounds differ markedly from their nonchlorinated counterparts, those of the species dealt with here are included in this section.

The compound nomenclature used is a most convenient extension of the IUPAC "*H*-nomenclature" for quasi-perhalogenated organic compounds.

Synthesis of Tetradecachlorotriphenylmethyl Radicals (X-PTM$^\bullet$). Method 1. From monosubstituted α*H*-tetradecachlorotriphenylmethanes, by conversion into the corresponding tetrachlorotriphenylmethides, followed by oxidation.[7b,14]

4*H*-Tetradecachlorotriphenylmethyl Radical (H-PTM$^\bullet$). This radical has been obtained from α*H*,4*H*-tetradecachlorotriphenylmethane (I) through its carbanion (H-PTM:$^-$) by two different procedures.[14,39] Reaction conditions: formation of carbanion I, 0.512 g; *n*-Bu_4N^+ HO^-, 0.60 mL of a 40% aqueous solution; THF, 15 mL; 2 h at room temperature. Oxidation to radical: addition of chloranil, 0.266 g; 1 h at room temperature. Yield, 95.8% (lit.[14] yield 73.3%).

4-Methyltetradecachlorotriphenylmethyl Radical (Me-PTM$^\bullet$). A mixture of α*H*-4-methyltetradecachlorotriphenylmethane (2.03 g), tetra-*n*-butylammonium hydroxide (2.1 mL, 40% aqueous solution), and THF (50 mL) was shaken at room temperature in an ultrasonic bath (30 min). Next, chloranil (1.02 g) was added and left for 1 h. By evaporation a residue was obtained which was dissolved in CCl_4 and submitted to flash chromatography in CCl_4/hexane, 1:1, through silica gel, resulting the pure title radical (1.89 g, 93%) (lit. (other method)[14] 80%). It was identified by IR and UV–vis spectra.

Perchlorotriphenylmethyl Radical (Cl-PTM$^\bullet$ or PTM$^\bullet$). It has been prepared from α*H*-pentadecachlorotriphenylmethane (II) by conversion into its carbanion (Cl-PTM:$^-$) by two different procedures. (a)[7b] Reaction conditions: formation of carbanion II, 7.6 g; NaOH, 7.0; DMSO, 90 mL; ethyl ether, 475 mL; 24 h at room temperature. Oxidation to radical: addition of I_2, 7.15 g; 24 h at room temperature. Yield 89% (literature, 81.6%). (b)[39] Formation of carbanion: II, 1.06 g; *n*-Bu_4N^+ HO^-, 1.4 mL of a 40% aqueous solution; THF, 45 mL; Oxidation to radical: addition of chloranil, 0.60 g; 24 h at room temperature. Yield 82.5% (unreported).

4-Bromotetradecachlorotriphenylmethyl Radical (Br-PTM$^\bullet$). A mixture of α*H*-4-carboxytetradecachlorotriphenylmethane (0.493 g, 6.4×10^{-4} mol), powdered NaOH (4 g), DMSO (50 mL), and ethyl ether (460 mL) was shaken (24 h) in the dark at room temperature. The mixture was filtered through a sintered-glass funnel into Br_2 (1.47 g, 9.2×10^{-3} mol) and left in the dark (24 h). The organic layer, after elimination of the excess of Br_2 ($NaHSO_3$, H_2O), and the 4-carboxytetradecachlorotriphenylmethyl radical (HO_2C-PTM$^\bullet$, formed with aqueous $NaHCO_3$), gave by evaporation the title radical in state of purity (0.101 g, 25% yield) (lit. (from radical I-PTM$^\bullet$),[14] 18.5%). It was identified by IR and UV–vis spectra.

Method 2. By acylation with 4-(chlorocarbonyl)tetradecachlorotriphenylmethyl radical (ClCO-PTM$^\bullet$). The preparation of the latter radical has been performed as described.[15]

4-Carbamoyltetradecachlorotriphenylmethyl radical (NH_2CO-PTM$^\bullet$): prepared as described in literature.[15]

4-(Dimethylcarbamoyl)tetradecachlorotriphenylmethyl Radical (Me_2NCO-PTM$^\bullet$). Through a solution of 4-(chlorocarbonyl)tetradecachlorotriphenylmethyl radical (ClCO-PTM$^\bullet$) (1.15 g, 1.46×10^{-3} mol) in THF, at 60 °C, a moderate stream of dimethylamine was passed (40 min). By evaporation, a garnet solid was obtained, which was dissolved in $HCCl_3$ and submitted to flash chromatography (silica gel) in this solvent. Recrystallization from CCl_4/hexane gave pure title radical (0.954, 82.2% yield): mp 183–186 °C; UV–vis ($CHCl_3$) 290 (sh), 335 (sh), 368 (sh), 383, 480 (sh), 510, 562 nm (ϵ 6300, 6300, 17 600, 34 500, 1075, 1100, 1075); IR (KBr) 2955, 2925, 2865, 1665, 1535, 1510, 1500, 1490, 1465, 1460, 1445, 1400, 1330, 1320, 1255, 1165, 1120, 1100, 810, 725, 705, 655, 645, 615, 605, 575, 530, 515; ESR data, Table I. Anal. Calcd for $C_{22}H_6Cl_{14}NO$: C, 33.2; H, 0.8; Cl, 62.3; N, 1.8. Found: C, 33.5; H, 1.0; Cl, 62.1; N, 1.6.

4-(Diphenylcarbamoyl)tetradecachlorotriphenylmethyl Radical (Ph_2NCO-PTM$^\bullet$). A mixture of 4-(chlorocarbonyl)tetradecachlorotriphenylmethyl radical (0.339 g, 4.3×10^{-4} mol), diphenylamine (0.65 g, 3.8×10^{-3} mol), triethylamine (0.5 mL), and toluene (6 mL) was shaken (30 min) at 120 °C. After cooling at room temperature, the precipitate of diphenylamine was filtered off. CCl_4 was added to the filtrate, and the mass was submitted to column chromatography in silica gel, eluting first with CCl_4 and next with $CHCl_3$. A red solid obtained was digested in refluxing ethyl ether. The microcrystalline red residue (0.224 g, 56.5% yield) was characterized as the title radical: mp 296–298 °C; UV–vis ($CHCl_3$) 270 (sh), 333 (sh), 365 (sh), 383, 485 (sh), 510, 560 nm (ϵ 10 500, 5900, 19 150, 38 600, 1440, 1510, 480); IR (KBr) 3070, 1673, 1590, 1485, 1450, 1365, 1330, 1320, 1300, 1257, 810, 770, 747, 725, 705, 693, 662, 650, 632, 605, 580, 525, 505 cm^{-1}; ESR data, Table I. Anal. Calcd for $C_{32}H_{10}Cl_{14}NO$: C, 41.7; H, 1.1; Cl, 53.9; N, 1.5. Found: C, 41.7; H, 1.1; Cl, 55.1; N, 1.5.

4-(Phenoxycarbonyl)tetradecachlorotriphenylmethyl Radical (PhOCO-PTM$^\bullet$). A mixture of 4-(chlorocarbonyl)tetradecachlorotriphenylmethyl radical (0.993 g, 1.26×10^{-3} mol), phenol (0.595 g, 6.32×10^{-3} mol), trimethylamine (1.4 mL), and anhydrous benzene (50 mL) was stirred (24 h) at room temperature. After evaporation, a red solid was obtained which was dissolved in CCl_4 and flash chroamtographed with this solvent through silica gel. The second fraction (0.80 g) was recrystallized from CCl_4/hexane, giving the title radical (0.675 g, 63.4% yield): mp 208–210 °C; UV–vis ($CHCl_3$) 285 (sh), 335 (sh), 365 (sh), 382, 480, 510, 562 nm (ϵ 6200, 6200, 18 300, 36 400, 1175, 1200, 1150); IR (KBr) 3050, 2920, 2840, 1760, 1595, 1585, 1530, 1500, 1482, 1468, 1375, 1326, 1312, 1300, 1285, 1265, 1250, 1212, 1190, 1175, 1148, 1120, 1100, 815, 805, 725, 720, 705, 685, 675, 658, 650, 630, 520, 505, 490 cm^{-1}; ESR data, Table I. Anal. Calcd for $C_{26}Cl_{14}H_5O_2$: C, 36.9; H, 0.6; Cl, 58.7. Found: C, 37.1; H, 0.6; Cl, 58.7.

Other Methods. 4-Methoxytetradecachlorotriphenylmethyl Radical (MeO-PTM$^\bullet$). (a) From perchlorofuchsone, as described.[11] Unreported UV–vis (C_6H_{12}) 383, 475 (sh), 510, 560

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[39] Armet, O.; Veciana, J.; Rovira, C.; Riera, J.; Castañer, J.; Molins, E.; Rius, J.; Miravitlles, C.; Olivella, S.; Brichfeus, J. *J. Phys. Chem.* **1987**, *95*, 5608.

nm (ε 37 500, 1100, 1200, 1250). (b) A mixture of tetra-*n*-butylammonium 4-methoxytetradecachlorotriphenylmethide, described later (0.051 g, 6.8 × 10^{-5} mol), I_2 (0.02 g), and THF (20 mL) was shaken (2 h) at room temperature. After elimination of the excess of I_2, the mass was extracted with $CHCl_3$, concentrated to a small volume, and submitted to preparative silica gel TLC and developed first with hexane and next with hexane/CCl_4, 1:1, to give the title radical (0.036 g, 93.3% yield). It was identified by IR[11] and UV-vis spectra.

4-(Methoxycarbonyl)tetradecachlorotriphenylmethyl Radical (MeOCO-PTM•). A mixture of tetra-*n*-butylammonium 4-(methoxycarbonyl)tetradecachlorotriphenylmethide (0.065 g, 6.3 × 10^{-5} mol), described later, I_2 (0.09 g), and ethyl ether (25 mL) was left undisturbed for 24 h. After destruction of the excess of I_2 ($NaHSO_3$, H_2O), the organic layer was evaporated to dryness, giving the title radical in state of purity (0.040 g, 81%g yield) (lit. (from α*H*-4-(methoxycarbonyl)tetradecachlorotriphenylmethane)[14] 85.4%). It was identified by melting point and IR spectrum.

4-Aminotetradecachlorotriphenylmethyl radical (NH_2-PTM•): from perchlorotriphenylcarbenium hexachloroantimonate, as described.[11]

Synthesis of Tetra-*n*-butylammonium Tetradecachlorotriphenylmethides. Method 1: from α*H*-tetradecachlorotriphenylmethanes, with tetra-*n*-butylammonium hydroxide, in THF. General procedure: To a solution of the αH compound (2.5 × 10^{-4} to 1.2 × 10^{-3} mol) in THF (10–45 mL) an excess of tetra-*n*-butylammonium hydroxide is added, and the mixture is shaken in an ultrasonic bath (2 h) at room temperature. The solution is poured onto a 1:1 mixture of hexane/water (50–100 mL), hand-shaken, and centrifuged. The oily bottom layer, after being washed with the hexane/water mixture, is dissolved in THF, and some hexane or hexane–ethyl ether is added to assist complete THF elimination by evaporation, which is performed under vacuum at 70 °C. The solid residue is pure, microcrystalline carbanion salt.

Tetra-*n*-butylammonium 4*H*-tetradecachlorotriphenylmethide (*n*-Bu_4N^+ H-PTM:$^-$): yield, 84%; dark-garnet solid; mp 163–165 °C; UV-vis (THF) 510 nm (ε 31 900); IR (KBr) 3090, 2960, 2930, 2875, 1535, 1510, 1498, 1470, 1415, 1362, 1330, 1280, 1210, 1162, 1150, 1020, 1010, 920, 870, 855, 800, 720, 715, 688, 680, 645, 608, 570, 505, 495 cm^{-1}. Anal. Calcd for $C_{35}H_{37}Cl_{14}N$: C, 43.4; H, 3.9; Cl, 51.3; N, 1.4. Found: C, 43.4; H, 3.9; Cl, 50.9; N, 1.7.

Tetra-*n*-butylammonium 4-methyltetradecachlorotriphenylmethide (*n*-Bu_4N^+ Me-PTM:$^-$): yield 95% (see method 2).

Tetra-*n*-butylammonium 4-(methoxyformyl)tetradecachlorotriphenylmethide (*n*-Bu_4N^+ MeOCO-PTM:$^-$): yield, 91% dark-garnet solid; mp 87–92 °C; UV-vis (THF) 515 nm (ε 32 600); IR (KBr) 2960, 2930, 2875, 1727, 1630, 1540, 1510, 1480, 1460, 1382, 1360, 1330, 1300, 1275, 1235, 1210, 1189, 1120, 1098, 1060, 1020, 968, 890, 875, 808, 790, 720, 698, 682, 658, 635, 610, 578, 525, 512 cm^{-1}. Anal. Calcd for $C_{37}H_{35}Cl_{14}NO_2$: C, 43.3; H, 3.8; Cl, 48.4; N, 1.4. Found: C, 43.7; H, 3.9; Cl, 48.3; N, 1.3.

Tetra-*n*-butylammonium perchlorotriphenylmethide (*n*-Bu_4N^+ Cl-PTM:$^-$ or PTM:$^-$): yield, 85.2% (see method 2).

Tetra-*n*-butylammonium 4-carboxylatotetradecachlorotriphenylmethide (*n*-Bu_4N^+ $^-$OCO-PTM:$^-$): yield 89%; dark-garnet solid; mp 92–96 °C; UV-vis (THF) 500 (sh), 523 nm (ε 24 000, 25 100); IR (KBr) 2960, 2930, 2875, 1615, 1540, 1515, 1500, 1480, 1458, 1360, 1278, 1220, 1208, 1150, 1125, 1105, 1065, 1022, 880, 802, 755, 742, 720, 710, 685, 670, 635, 610, 580, 530, 515 cm^{-1}. Anal. Calcd for $C_{52}H_{72}Cl_{14}N_2O_2$: C, 49.8; H, 5.8; Cl, 39.6; N, 2.2. Found: C, 49.5; H, 5.8; Cl, 39.2; N, 2.4.

Method 2: As in method 1, but substituting the triphenylmethyl radical for the α*H*-triphenylmethane.

Tetra-*n*-butylammonium 4*H*-tetradecachlorotriphenylmethide (*n*-Bu_4N^+ *H*-PTM:$^-$): yield, 88% (see method 1).

Tetra-*n*-butylammonium 4-methyltetradecachlorotriphenylmethide (*n*-Bu_4N^+ Me-PTM:$^-$): yield, 95%; dark-garnet solid; mp 98–102 °C; UV-vis (THF) 276 (sh), 517 nm (ε 11 300, 27 200); IR (KBr) 2970, 2940, 2880, 1545, 1510, 1502, 1485, 1390, 1365, 1340, 1280, 1220, 1205, 1138, 1060, 1030, 1025, 800, 718, 685, 670, 645, 630, 610, 515 cm^{-1}. Anal. Calcd for $C_{38}H_{39}Cl_{14}N$: C, 44.0; H, 4.0; Cl, 50.5; N, 1.4. Found: C, 44.3; H, 4.1; Cl, 49.6; N, 1.4.

Tetra-*n*-butylammonium perchlorotriphenylmethide (*n*-Bu_4N^+ Cl-PTM:$^-$ or PTM:$^-$): yield, 91%; dark-garnet solid; mp 155–159 °C; UV-vis (THF) 513 nm (ε 33 800); IR (KBr) 2960, 2875, 1495, 1478, 1455, 1408, 1365, 1325, 1275, 1218, 1202, 1148, 1018, 878, 800, 732, 720, 685, 680, 645, 638, 608, 575, 515 cm^{-1}. Anal. Calcd for $C_{35}H_{36}Cl_{15}N$: C, 41.9; H, 3.6; Cl, 53.0; N, 1.4. Found: C, 41.9; H, 3.5; Cl, 52.9; N, 1.5.

Tetra-*n*-butylammonium 4-methoxytetradecachlorotriphenylmethide (*n*-Bu_4N^+ MeO-PTM:$^-$): yield, 86.4%; dark-garnet solid; mp 153–156 °C; UV-vis (THF) 510 nm (ε 26 100); IR (KBr) 2960, 2930, 2870, 1560–1538, 1513, 1498, 1487, 1475, 1462, 1452, 1440, 1375–1355, 1345–1325, 1275, 1215, 1200, 1145, 1015, 992, 905, 877, 840, 796, 730, 720, 713, 692, 678, 658, 638, 630, 605, 575, 535, 522 cm^{-1}. Anal. Calcd for $C_{36}H_{39}Cl_{14}ON$: C, 43.3; H, 3.9; Cl, 49.7; N, 1.4. Found: C, 43.9; H, 4.1; Cl, 48.6; N, 1.3.

Tetra-*n*-butylammonium 4-aminotetradecachlorotriphenylmethide (*n*-Bu_4N^+ NH_2-PTM:$^-$): yield, 88%; dark-brown solid; mp 111–114 °C; UV-vis (THF) 336 (sh), 521, 645 (sh), 772 nm (ε 10 500, 11 300, 8300, 13 000); IR (KBr) 3500, 3400, 2970, 2940, 2880, 1600, 1535, 1510, 1495, 1480, 1375, 1358, 1340, 1330, 1270, 1245, 1220, 1210, 1148, 1105, 1015, 980, 935, 870, 860, 850, 810, 800, 730, 720, 707, 690, 680, 657, 645, 605, 580, 540, 530 cm^{-1}. Anal. Calcd for $C_{35}H_{38}Cl_{14}N_2$: C, 42.8; H, 3.9; Cl, 50.5; N, 2.8. Found: C, 42.8; H, 4.1; Cl, 50.5; N, 2.5.

Tetra-*n*-butylammonium 4-bromotetradecachlorotriphenylmethide (*n*-Bu_4N^+ Br-PTM:$^-$): yield, 78%; dark-garnet solid; mp 157–160 °C; UV-vis (THF) 515 nm (ε 33 400); IR (KBr) 2960, 2930, 2875, 1500, 1478, 1470, 1455, 1360, 1325, 1300, 1270, 1218, 1203, 1100, 1055, 1015, 875, 800, 780, 732, 718, 688, 655, 645, 630, 605, 578, 512 cm^{-1}. Anal. Calcd for $C_{35}H_{35}Cl_{14}BrN$: C, 40.1; H, 3.5; Cl, 47.4; Br, 7.6; N, 1.3. Found: C, 39.8; H, 3.4; Cl, 47.2; Br, 7.5; N, 1.5.

Tetra-*n*-butylammonium 4-carbamoyltetradecachlorotriphenylmethide (*n*-Bu_4N^+ NH_2CO-PTM:$^-$): yield, 87.8%; dark-garnet solid; mp 104–106 °C; UV-vis (THF) 280 (sh), 513 nm (ε 9750, 28 000); IR (KBr) 3470, 3390, 2960, 2930, 2875, 1680, 1585, 1540, 1510, 1480, 1403, 1355, 1325, 1270, 1215, 1205, 1020, 870, 800, 730, 715, 682, 657, 640, 630, 607, 530, 510 cm^{-1}. Anal. Calcd for $C_{36}H_{38}Cl_{14}N_2O$: C, 42.8; H, 3.8; Cl, 49.1; N, 2.8. Found: C, 43.1; H, 3.8; Cl, 48.9; N, 2.8.

Tetra-*n*-butylammonium 4-(dimethylcarbamoyl)tetradecachlorotriphenylmethide (*n*-Bu_4N^+ Me_2NCO-PTM:$^-$): yield, 63%; dark-garnet solid; mp 100–103 °C; UV-vis (THF) 276 (sh), 515 nm (ε 8250, 35 000); IR (KBr) 2960, 2930, 2870, 1650, 1645, 1568, 1540, 1512, 1502, 1478, 1400, 1367–1353, 1330, 1280, 1260, 1218, 1205, 1160, 1018, 870, 800, 730, 715, 697, 680, 655, 645, 630, 600, 580, 525, 510 cm^{-1}. Anal. Calcd for $C_{38}H_{42}Cl_{14}N_2O$: C, 43.9; H, 4.1; Cl, 47.8; N, 2.7. Found: C, 44.2; H, 4.1; Cl, 47.1; N, 2.7.

Tetra-*n*-butylammonium 4-(diphenylcarbamoyl)tetradecachlorotriphenylmethide (*n*-Bu_4N^+ Ph_2NCO-PTM:$^-$): yield, 90.7%; dark-garnet solid; mp 109–112 °C; UV-vis (THF) 275 (sh), 517 nm (ε 11 500, 34 800); IR (KBr) 3065, 3055, 2960, 2930, 2875, 1660, 1595, 1540, 1510, 1490, 1450, 1395, 1355, 1325, 1300, 1270, 1220, 1205, 1180, 1165, 1070, 1030, 1020, 870, 800, 772, 748, 725, 715, 690, 680, 657, 647, 630, 600, 577, 523, 502 cm^{-1}. Anal. Calcd for $C_{48}H_{46}Cl_{14}ON_2$: C, 49.6; H, 4.0; Cl, 42.7; N, 2.4. Found: C, 49.6; H, 4.1; Cl, 42.9; N, 2.4.

Tetra-*n*-butylammonium 4-(phenoxycarbonyl)tetradecachlorotriphenylmethide (*n*-Bu_4N^+ PhOCO-PTM:$^-$): yield, 89.7%; dark-garnet solid, mp 90–93 °C; UV-vis (THF) 276 (sh), 515 nm (ε 13 500, 35 000); IR (KBr) 2960, 2930, 2870, 1748, 1620–1650, 1592, 1540, 1510, 1490, 1480, 1455, 1390, 1358, 1327, 1295, 1220, 1205, 1125, 1153, 1110, 1087, 1017, 1000, 732, 720, 715, 705, 695, 680, 652, 632, 602, 575, 520, 508, 500 cm^{-1}. Anal. Calcd for $C_{42}H_{41}Cl_{14}NO_2$: C, 46.4; H, 3.9; N, 1.3. Found: C, 46.7; H, 3.9; N, 1.2.

The Single-Electron Transfers. The solvent was anhydrous THF. The reactions were performed in air at room temperature (≈20 °C), using freshly prepared carbanion salts and their solutions. The initial concentrations of X-PTM• and S-PTM• were of the order of 2 × 10^{-4} mol L^{-1}, and the initial molar ratios, [X-PTM:$^-$]/[S-PTM•] and [S-PTM:$^-$]/[X-PTM•], varied from 1 to 5 or 10, approximately. They have been carried out by mixing the solution of the radical with another of the carbanion salt and taking the ESR spectrum immediately.

The Analytical Method. The SETs have been monitored up to 3 h by ESR spectrometry and have been reproduced twice at least. The relative percentages of starting and ensuing radicals have been calculated from the experimental ESR curve by computer simulation, the input data being the individual parameters of the two radicals involved, linewidths, Gaussian contributions to line shape, hyperfine coupling constants, and Landé's *g* values, as well as those dealing with the spectrum format—magnetic range and gain factor—which allow excellent iterative matching of the experimental and simulated spectra.

The ESR spectra of monosubstituted PTM radicals consist of a main single line, and very weak, symmetrically positioned pairs of satellite lines due to the hyperfine couplings with one (central) α, three bridgehead, and six ortho ^{13}C nuclei in natural abundance.[7e,40] Since in THF the main lines of the radicals have similar widths (half-width: 1.2–1.5 G), accurate simulation can only be effected if the ESR spectrum of at least one of the two radicals present in the resulting reaction mixture displays more than one main line. This is the reason for selecting radical H-PTM$^\bullet$ (two lines of equal intensities, due to coupling with the para proton; hfc = 1.93 G[7c,14] [Figure 1, A]) and Me-PTM$^\bullet$ (four lines of relative intensities 1:3:3:1 due to the three methyl protons; hfc = 2.15 G[7c,14] [Figure 1, S]) as two *standards*.

For optimal spectral curve fitting and, consequently, superior accuracy, two expanded ESR recording scales (10 G, for H-PTM$^\bullet$; 16 G, for Me-PTM$^\bullet$) have been employed. Thus in practically all cases an exact reproduction of the experimental ESR curve for the binary mixture is reached. The analyses giving percentages of the standard radical outside the 10–90% range have usually been disregarded because of the high intrinsic error involved. In the intermediate range estimated error in component composition is about ±2%. The accuracy of the simulation method has been checked with mixtures of pure X-PTM$^\bullet$ and S-PTM$^\bullet$ radicals. The resulting data is given in Table V (supplementary material).

The SET reactions on a *semimicroscale* have been performed as follows: To a solution of radical in THF an equimolecular amount of solid carbanion salt is added, and the resulting solution is stirred for hours at room temperature. Drops of aqueous HCl are added until the color shifts from deep garnet to deep red. Volatile parts are eliminated in vacuo, and the residue is submitted to preparative TLC (silica gel; hexane). The first strip consists in a mixture of the less polar radical and its αH compound, and the second fraction, a mixture of the remaining radical and its αH compound. The analyses are accomplished by IR (component identification) and UV–vis (radical/αH compound ratio).

MeO-PTM$^\bullet$/H-PTM:$^-$ SET R. Starting components: 4-methoxytetradecachlorotriphenylmethyl radical (MeO-PTM$^\bullet$), 0.054 g (7.2 × 10^{-5} mol); tetra-*n*-butylammonium 4*H*-tetradecachlorotriphenylmethide (*n*-Bu$_4$N$^+$ H-PTM:$^-$), 0.069 g (7.2 × 10^{-5} mol); THF (20 mL). Reaction time: 2 h. Yields (%): H-PTM$^\bullet$, 37; MeO-PTM$^\bullet$, 65. Mass balance: 97%. **H-PTM$^\bullet$/MeO-PTM:$^-$ SET L.** Starting components: H-PTM$^\bullet$, 0.056 g (7.7 × 10^{-5} mol); tetra-*n*-butylammonium 4-methoxytetradecachlorotriphenylmethide (*n*-Bu$_4$$^+$ MeO-PTM:$^-$), 0.079 g (7.9 × 10^{-5} mol); THF, 20 mL. Reaction time: 2 h. Yields (%): H-PTM$^\bullet$, 36.5; MeO-PTM$^\bullet$, 65.5. Mass balance: 90%.

MeO-PTM$^\bullet$/Cl-PTM:$^-$ SET R. (a) Starting components: MeOPTM$^\bullet$, 0.040 g (5.3 × 10^{-5} mol); tetra-*n*-butylammonium perchlorotriphenylmethide (*n*-Bu$_4$N$^+$ Cl-PTM:$^-$), 0.052 g (5.2 × 10^{-5} mol); THF (20 mL). Reaction time: 2 h. Yields (%): Cl-PTM$^\bullet$, 23.4; MeO-PTM$^\bullet$, 74. Mass balance: 91.5%. (b) Starting components: MeO-PTM$^\bullet$, 0.039 g (5.25 × 10^{-5} mol); *n*-Bu$_4$N$^+$ Cl-PTM:$^-$, 0.053 g (5.3 × 10^{-5} mol); THF (20 mL). Reaction time: 24 h. Yields (%): Cl-PTM$^\bullet$, 25; MeO-PTM$^\bullet$, 73. Mass balance: 95%. **Cl-PTM$^\bullet$/MeO-PTM$^-$ SET L.** (a) Starting components: tetradecachlorotriphenylmethyl radical (Cl-PTM$^\bullet$), 0.037 g (4.9 × 10^{-5} mol); *n*-Bu$_4$N$^+$ MeO-PTM:$^-$, 0.052 g, (5.2 × 10^{-5} mol); THF (20 mL). Reaction time: 2 h. Yields (%): Cl-PTM$^\bullet$, 26; MeO-PTM$^\bullet$, 76. Mass balance: 85%. (b) Starting components: Cl-PTM$^\bullet$, 0.037 g (4.9 × 10^{-5} mol); *n*-Bu$_4$N$^+$ MeO-PTM:$^-$, 0.052 g (5.2 × 10^{-5} mol); THF (20 mL). Reaction time: 24 h. Yields (%): Cl-PTM$^\bullet$, 24.5; MeO-PTM$^\bullet$, 75.5. Mass balance: 90%.

The Osmometric Measurements. Mean molecular weight (MMW) determinations, by vapor pressure osmometry in THF (45 °C), have been performed on carbanion salts and their mixtures, on radicals and their mixtures, and on carbanion salt/radical (1:1) mixtures. The molar concentrations were about 8 × 10^{-3} mol L^{-1}, i.e., 40 times those of the SETs runs, approximately. The resulting data are shown in Table IV.

Acknowledgment. In spite that further research on the abnormal SET behavior here described is needed, for nonscientific reasons, the present research line on SETs between inert free radicals and stable carbionic species is going to be discontinued. We wish to encourage other research groups to carry on this most promising exploration and, consequently, are willing to provide them with any help they can. Also, we acknowledge the sponsorships received from the Spanish Higher Council for Scientific Research (CSIC) and from the "Comisión Asesora para la Investigación Científica y Técnica" (CAICYT), as well as extend our appreciation to Dr. J. Riera, Dr. C. Rovira, Dr. J. Castañer, J. Vidal, A. Díez, and Dr. E. Molins for their assistance. I.P. wishes to express her gratitude to the Spanish Ministry of Education and Science for a doctoral fellowship during the period 1984–1989.

Registry No. Q$^+$Me-PTM$^-$, 126062-13-3; Q^{+-}OCO-PTM$^-$, 126061-88-9; Q$^+$NH$_2$-PTM$^-$, 126061-90-3; Q$^+$MeO-PTM$^-$, 126061-92-5; Q$^+$NH$_2$CO-PTM$^-$, 126061-94-7; Q$^+$Ph$_2$NCO-PTM$^-$, 126061-96-9; Q$^+$MeOCO-PTM$^-$, 126061-98-1; Q$^+$Me$_2$NCO-PTM$^-$, 126062-00-8; Q$^+$Cl-PTM$^-$, 126062-01-9; Q$^+$Br-PTM$^-$, 126062-03-1; Q$^+$PhOCO-PTM$^-$, 126062-05-3; Q$^+$H-PTM$^-$, 126062-07-5; H-PTM$^\bullet$, 79855-13-3; Me-PTM$^\bullet$, 79855-18-8; MeO-PTM$^\bullet$, 71947-01-8; NH$_2$CO-PTM$^\bullet$, 86822-11-9; Ph$_2$NCO-PTM$^\bullet$, 126062-08-6; MeOCO-PTM$^\bullet$, 79855-14-4; Me$_2$NCO-PTM$^\bullet$, 126062-09-7; Cl-PTM$^\bullet$, 4070-01-3; Br-PTM$^\bullet$, 79855-16-6; PhOCO-PTM$^\bullet$, 126062-10-0; $^-$OCO-PTM$^\bullet$, 126062-11-1; ClCO-PTM$^\bullet$, 77225-19-5; α*H*-4-methyltetradecachlorotriphenylmethane, 79839-38-6; α*H*-4-carboxytetradecachlorotriphenylmethane, 79839-41-1.

Supplementary Material Available: Table V, containing detailed data for Table II (3 pages). Ordering information is given on any current masthead page.

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