

Oxidation of the Perchlorotriphenylmethyl Radical to the Carbocation, and Its Unique Abrupt Reversion

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A solution of AlCl_3 in CH_2Cl_2 reacts slowly, at room temperature, with perchlorotriphenylmethyl radical (PTM^\bullet), an inert carbon free radical, to give perchlorotriphenylmethyl cation (PTM^+) quantitatively. However, by gradual addition of CH_2Cl_2 into the resulting solution a point is reached where the PTM^+ reverts to PTM^\bullet instantaneously and quantitatively. A mechanism for this exceptional phenomenon is suggested. Some PTM^+ reactions, namely hydrolysis yielding quinonoid species and single-electron transfers with hydride ion donors, are reported and discussed.

Introduction

The “inert free radicals” (IFR) are completely disassociated trivalent-carbon species provided with a unique chemical passivity due to an about full steric blockage of their molecular sites where most of the *spin* density resides, provided by persubstitution by chlorine. Their extrapolated half-lives in solution in air, at room temperature, are of the order of one-hundred years. Also, they withstand aggressive chemicals and high temperatures unlike most conventional tetravalent-carbon compounds and materials.^{1–4} Nevertheless, they are active in single-electron processes.^{5–11}

Solutions of anhydrous AlCl_3 in methylene chloride oxidize ethylenes and aromatic compounds to their radical cations.^{12,13} This prompted the authors to investigate the behavior of that reagent vs perchlorotriphenylmethyl radical (PTM^\bullet), a paradigm of an inert free radical.

Results and Discussion

Cationization of the Perchlorotriphenylmethyl Radical (PTM^\bullet). The UV–visible spectrum of a saturated solution of AlCl_3 in CH_2Cl_2 displays an intense peak

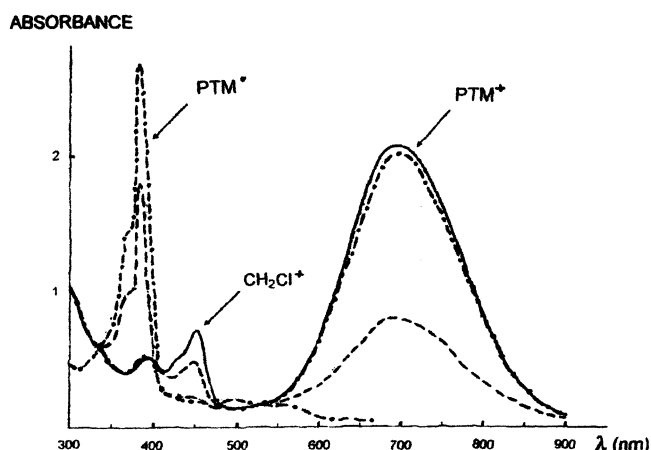


FIGURE 1. UV–vis spectrum. Progress of the conversion of PTM^\bullet to PTM^+ in $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$, at 20 °C. Times: 0 (• – •), 15 (– –), 45 (• – • –), and 105 (–) min.

at 450 nm (Supporting Information, Figure S1) assigned to carbocation CH_2Cl^+ . Upon addition of radical PTM^\bullet this peak disappears immediately to reappear a few minutes later (Figure 1) along those of PTM^\bullet (385 nm,¹) and the perchlorotriphenylmethyl cation (PTM^+ ; 690 nm),^{9,11,14} the solution changing from red (radical) to deep-green (carbocation). The progress of that one-electron oxidation has been followed either by the decrease of the PTM^\bullet UV–vis peak¹ or the increase of that of PTM^+ (Figure 1). The reaction is virtually complete in about 100 min. Beyond that time (hours) a colossal increase of the 450-nm peak is observed (Supporting Information, Figure S2). A highly polar solution results when the reaction is over.

These and other results to be reported next are consistent with the following mechanism: cation CH_2Cl^+ , formed by reaction of the solvent with the AlCl_3 , would react (SET) with PTM^\bullet to give PTM^+ .

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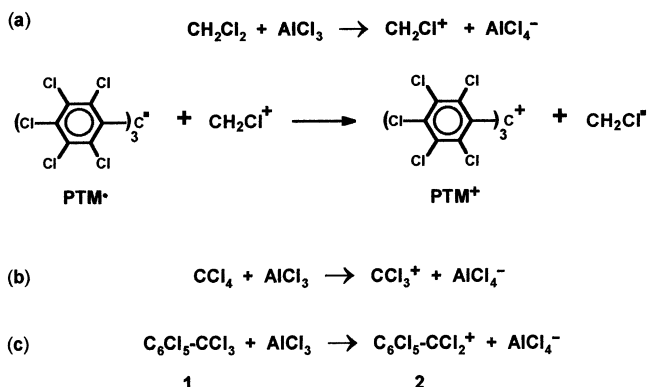
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It is reasonable that molecules of salt $\text{CH}_2\text{Cl}^+ \text{AlCl}_4^-$ associate with the PTM^+ ions as they are formed giving supramolecular species (SMS) which provide stability and an effective steric/ionic shield to PTM^+ against electron donors (next section).

The rate of formation of PTM^+ is accelerated by addition (1:25) of carbon tetrachloride or perchlorotoluene (1), the half-reaction time (20 °C) falling from 19 to 10 and 2 min, respectively (Supporting Information, Figures S3 and S4). This is assigned to the formation of CCl_3^+ or perchlorobenzyl cation (2),^{3a} respectively, their activity as one-electron acceptors, giving trichloromethyl and perchlorobenzyl¹⁵ radicals, overriding that of CH_2Cl^+ .

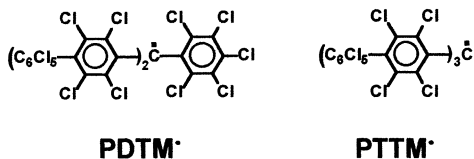
The rate of cationization is enhanced also by Cl_2 , this being attributed to $\text{AlCl}_3/\text{Cl}_2$ positive-chlorine complexes behaving as additional one-electron oxidants.

The enhancements due to CCl_4 and perchlorotoluene are evidenced respectively in Supporting Information Figures SI, S2, and S3.

The cationization of PTM^+ with AlCl_3 in chlorobenzene does not occur. However, addition of perchlorotoluene (1) allows it.

It is mentioned that carbocation 2 had been postulated as the intermediate in the condensation of chlorocarbon 1 with trichloroethylene in $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$, with CaCl_2 or LiCl added.^{3a}

$\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ converts perchloro-4,4'-diphenyltriphenylmethyl (PDTM^+) and perchloro-4,4',4''-triphenyltriphenylmethyl (PTTM^+) radicals^{16a} into the corresponding carbocations, as reagent $\text{AlCl}_3/\text{SO}_2\text{Cl}_2$ does.^{16b}



Reversions of PTM^+ to PTM^+ : (a) Adding CH_2Cl_2 .

By dropwise addition of purified CH_2Cl_2 into the deep-green solution of PTM^+ , obtained from radical PTM^+ with $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ at room temperature, a point is reached where suddenly the solution turns bright red due to a quantitative reversion to PTM^+ , as ascertained by the UV-vis spectrum and radical isolation. However, when

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the dilution is effected with CH_2Cl_2 saturated with anhydrous AlCl_3 instead, no reversion occurs.

That is accounted for as follows: The gradual addition of CH_2Cl_2 lowers the polarity and retrogrades the stabilizing salt $\text{CH}_2\text{Cl}^+ \text{AlCl}_4^-$ to its neutral components. Consequently, a point is reached where highly aggressive PTM^+ is liberated from the SMS, reacting with CH_2Cl_2 to afford PTM^+ and transient carbocation-radical $[\text{CH}_2\text{Cl}_2]^{\bullet+}$ in an extremely high rate. Tunneling is likely to be involved.¹⁷

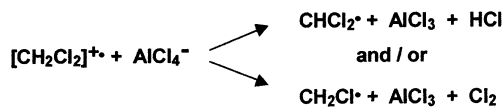
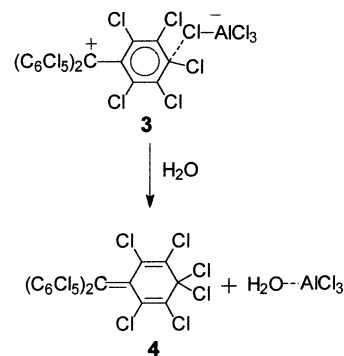


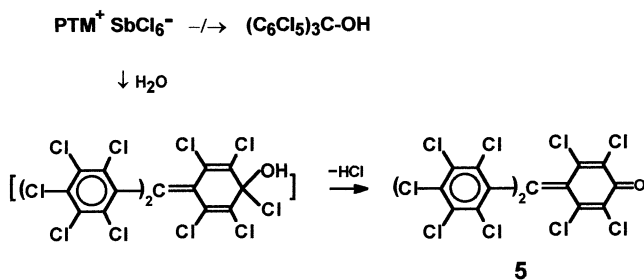
Figure 2 is a synopsis of the suggested mechanisms involved.

(b) Adding Water. Addition of water to the solution of PTM^+ in $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$, at room temperature causes a nearly quantitative reversion to PTM^+ . This is consistent with the preceding explanation, since water reacts with the AlCl_3 component of the SMS. However, when the treatment is performed at 0 °C, although some (24%) of the PTM^+ is formed, the major product becomes perchlorodiphenylmethylenecyclohexa-1,4-diene (PTM-Cl , 4) (72%; peak at 372 nm¹⁰), suggesting the initial existence of chlorine bridging between counterion AlCl_4^- and a PTM^+ para-position.



Quinonoid chlorocarbon 4 is also obtained in excellent yield by adding water to PTM^+ in $\text{AlCl}_3/\text{SO}_2\text{Cl}_2$, at low temperature.¹⁰

Hydrolytic treatment of a solution of $\text{PTM}^+ \text{SbCl}_6^-$ in SO_2Cl_2 (or CCl_4) gives perchlorofuchson (5) instead,¹⁰ neither chlorocarbon 4 nor perchlorotriphenylcarbinol being formed. The failure to give the latter is attributed to the absence of that chlorine bridging between PTM^+ and SbCl_6^- and to steric shielding of the PTM^+ α position, respectively.



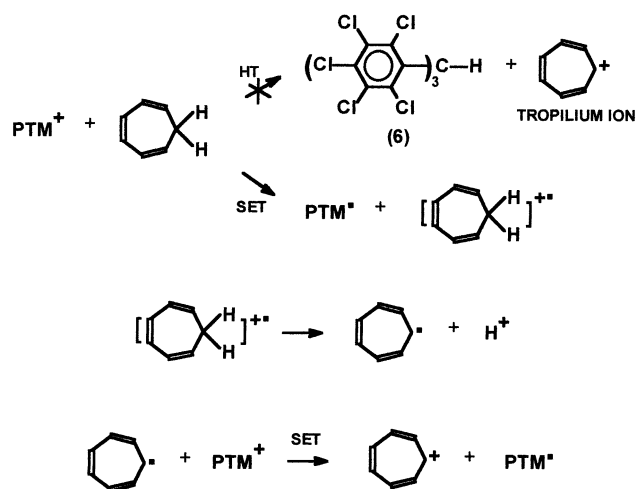
(c) **Adding Dioxane.** A quantitative yield of PTM^\bullet (UV-vis) results when dioxane is added to the solution of PTM^+ in $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$. Since dioxane forms strong complexes with AlCl_3 ,¹⁸ it is also a SMS breaker.

Quinonoid chlorocarbon **4** reacts with $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$, yielding PTM^+ quantitatively.¹⁰ Subsequent addition of a small amount of dioxane results in the formation of PTM^\bullet . However, in the presence of Cl_2 , **4** is recovered.

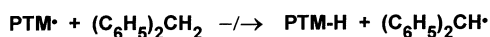
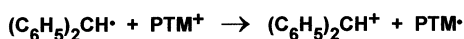
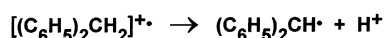
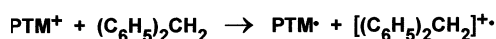
Reactions with Hydride Ion Donors. (a) With Cycloheptatriene. It has been reported that $\text{PTM}^+ \text{SbCl}_6^-$ reacts with cycloheptatriene giving PTM^\bullet ¹⁴ instead of expected αH -pentadecachlorotriphenylmethane (**6**, PTM-H).⁹ Similarly, PTM^+ in $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ reacts with cycloheptatriene, at room temperature, giving **6** (99.5%).

However, the reaction of related perchlorodiphenylmethyl hexachloroantimonate ($\text{PDM}^+ \text{SbCl}_6^-$) with cycloheptatriene takes place in the conventional way, giving αH -undercachlorodiphenylmethane ($(\text{C}_6\text{Cl}_5)_2\text{CHCl}$) and tropylium hexachloroantimonate ($\text{C}_7\text{H}_7^+ \text{SbCl}_6^-$).¹⁹

Those results suggest that at least some hydride shifts from hydride donors take place stepwise: (a) capture of one electron from cycloheptatriene, giving perchlorodiphenylmethyl radical (PDM^\bullet) and radical cation $\text{C}_7\text{H}_8^{+\bullet}$, and (b) release of a hydrogen atom from the latter to the PDM^\bullet . This two-step process had been proposed as a general mechanism for the hydride ion shifts.^{3c,19} In the case of PTM^+ , step b does not take place because of severe steric shielding of its tricovalent α -carbon by six butressed ortho chlorines, hindering the subsequent hydrogen atom transfer from radical cation $\text{C}_7\text{H}_8^{+\bullet}$ to PTM^\bullet .



(b) **With Diphenylmethane.** Diphenylmethane performs like cyclohexatriene, giving PTM^\bullet (93%).



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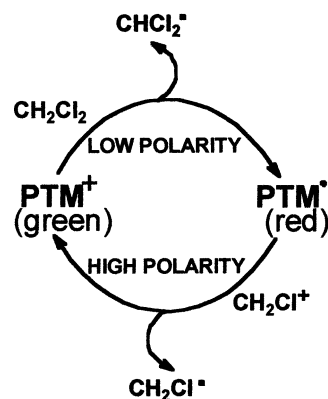


FIGURE 2. Suggested mechanism for the processes involved in system $\text{PTM}^\bullet/\text{PTM}^+/\text{AlCl}_3/\text{CH}_2\text{Cl}_2$. Synopsis.

Cationization by Other Lewis Acids. Under conditions similar to those reported here, anhydrous FeCl_3 in CH_2Cl_2 (room temperature; ultrasonics, argon, 2 h) converts PTM^\bullet into PTM^+ . Addition of water to the resulting solution gives PTM^\bullet (86%) and perchlorofuchsonone (**5**) (5%). SnCl_4 , TiCl_4 , SbCl_3 , and AlF_3 are ineffectual.

A Final Remark. It is pointed out that some reactions, processes, and phenomena encountered and reported here could hardly occur, even detected, outside the domain of the perchloro-organic chemistry.

Experimental Section

Starting Materials. Perchlorotriphenylmethyl radical (PTM^\bullet) and perchlorotoluene (**1**)²⁰ were prepared as described in the literature.

Cationization of the Perchlorotriphenylmethyl Radical (PTM^\bullet) with $\text{CH}_2\text{Cl}_2/\text{AlCl}_3$ (Figure 1). To a solution of PTM^\bullet (4.82×10^{-3} g) in purified CH_2Cl_2 (50 mL), at 20 °C, in argon, was added an excess of ground anhydrous AlCl_3 , and the mixture was shaken with ultrasonics. After a short induction period an increasingly intense deep-green color appeared. The UV-vis spectrum of the supernatant solution was taken at various times. After 105 min the formation of perchlorotriphenylmethyl cation (PTM^+) was 99%, as ascertained by comparison with the UV-vis spectrum of $\text{PTM}^+ \text{SbCl}_6^-$ (band at 690 nm).¹⁴

Other Cationizations of PTM^\bullet . (a) With Cl_2 Added. A solution of PTM^\bullet (0.193 g, 2.53×10^{-4} mol) in CH_2Cl_2 (50 mL) was saturated with chlorine at room temperature, and an excess of finely ground anhydrous AlCl_3 (1.87 g) was added next. The resulting mass was shaken with ultrasonics (1 h). The ESR spectrum of the deep-green supernatant solution indicated that 95% of the initial PTM^\bullet had disappeared, while the UV-vis spectrum (after dilution with CH_2Cl_2 saturated with AlCl_3) showed that the formation of PTM^+ was 98% of theory. Next, a few drops of dioxane was added and the white AlCl_3 -dioxane white complex formed was filtered off. By evaporation of the resulting filtrate quinonoid chlorocarbon **4** was obtained (86%), being identified by IR and UV-vis spectra.¹⁰

(b) With CCl_4 Added. To a solution of PTM^\bullet (0.0501 g) in CH_2Cl_2 (25 mL) containing CCl_4 (1 mL), at 20 °C, was added finely ground anhydrous AlCl_3 . The resulting mixture was treated as in (a). Samples of the supernatant solution were

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taken at various times and their UV–vis spectra recorded. The conversion of PTM^\bullet to PTM^+ was complete in 35 min ($\tau_{1/2}$, 10 min).

(c) With Perchlorotoluene (1) Added. To a solution of PTM^\bullet (0.0481 g, 0.641×10^{-4} mol) and perchlorotoluene (0.0444 g, 1.21×10^{-4} mol) in CH_2Cl_2 (25 mL), at 20 °C, was added an excess of finely ground anhydrous AlCl_3 . The resulting mixture was treated as usual. The change in UV–vis absorption was monitored, the cationization being practically complete in 25 min ($\tau_{1/2}$, 2 min).

Reversions to PTM^\bullet . **(a) With CH_2Cl_2 .** To the resulting solution of PTM^+ , obtained as here described, was gradually added a comparable volume of purified CH_2Cl_2 , at room temperature, affording immediately PTM^\bullet quantitatively (UV–vis).

(b) With Water. (A) The green liquid phase containing cation PTM^+ , obtained as before (PTM^\bullet , 0.059 g, CH_2Cl_2 , 10 mL; excess of AlCl_3 ; 1 h), was poured onto water (5 mL), at room temperature. The resulting red mixture was extracted with ethyl ether. The ethereal layer was washed with water, dried with anhydrous Na_2SO_4 , and evaporated to dryness. Solid, 98% pure (UV–vis) PTM^\bullet was obtained. (B) The process was carried out as in (A) (PTM^\bullet , 0.051 g, CH_2Cl_2 , 10 mL, AlCl_3 , 0.113 g; 17 h). The resulting ice-cooled mixture, containing 0.06% of the initial PTM^\bullet (UV–vis), was filtered, and crushed ice was added to the filtrate. The organic layer was a mixture of PTM^\bullet (24%, UV–vis) and perchloro-2-(diphenylmethylene)-cyclohexa-1,4-diene (**4**)¹⁰ (72%; isolated).

(c) With Dioxane. To about 1 mL of the solution of PTM^+ , prepared as usual, was added two drops of dioxane, its green

color turning red immediately. The UV–vis spectrum of the resulting solution showed that the reversion to PTM^\bullet was quantitative.

(d) With Cycloheptatriene. To a solution of PTM^+ , prepared from PTM^\bullet (0.067 g) in CH_2Cl_2 (10 mL) as before, was added a few drops of cycloheptatriene. The resulting solution was poured onto diluted aqueous HCl and then extracted with ethyl ether. PTM^\bullet was obtained (99.5%) by evaporation.

(e) With Diphenylmethane. The treatment was effected as above (PTM^\bullet , 0.90 g, CH_2Cl_2 , 13 mL). PTM^\bullet was obtained (93%).

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Supporting Information Available: UV–visible absorbance spectra: cation CH_2Cl^+ in $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ (Figure S1); cationization of PTM^\bullet (Figure S2); progress of the cationization with additives CCl_4 (Figure S3) and perchlorotoluene (**1**) (Figure S4). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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