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Perchlorobis(1-indenyl) and Perchloro-1-indenyl Radical

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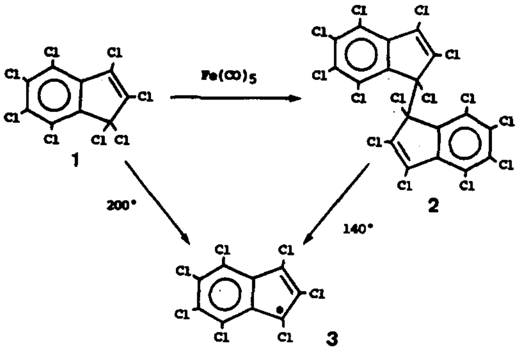
The synthesis of perchlorobis(1-indenyl) (2) is presented and its thermal behavior described. The perchloro-1-indenyl radical (3), in equilibrium with its dimer 2, has been detected by ESR spectroscopy. From a study of this equilibrium, the dissociation energy of 2 has been calculated to be 20.83 kcal·mol^{-1}.

Introduction

During the course of our investigations into highly strained alkaromatic chlorocarbons, we found that perchloro-1,2-diphenylethane is not an isolable compound. At room temperature it exists in an equilibrium with its homolysis product, the perchlorobenzyl radical, with the concentration of the latter being temperature dependent.[1]

We now wish to report the synthesis of the perchlorobis(1-indenyl) compound (2) and detection of the perchloro-1-indenyl radical (3) by ESR spectroscopy.



Results and Discussion

Carefully controlled dimerization of perchloroindene (1) by means of iron pentacarbonyl in refluxing benzene gives a high yield of perchlorobis(1-indenyl) (2), mp 206–8 °C with decomposition. However, in trichlorobenzene solution it begins to dissociate into perchloro-1-indenyl radical (3) at temperatures as low as 70 °C.

ESR. The ESR spectrum of the perchloro-1-indenyl radical (3) presents seven equally spaced lines with 1:2:3:4:3:2:1 relative intensities and a coupling constant of 2.1 G, along with small ^{13}C satellites (Figure 1a). This spectrum suggests interaction of the lone electron with two of the chlorines, presumably those at positions 1 and 3. Analogously, the ESR of indenyl radical presents a coupling constant (with the hydrogens in positions 1 and 3) of 11.8 G, much higher than those of the rest of the hydrogens (2.19, 2.19, and 1.49 G).[2] In radical 3 the coupling constants corresponding to the remaining chlorines do not appear in the spectrum and serve only to contribute to the broadening of the line widths of the peaks (1.2 G), as occurs in perchlorobenzyl radical.[1] The coupling constant with the 1- and 3-chlorines in 3 (2.1 G)[3] is smaller than that with the α-chlorines in perchlorobenzyl (3.0 G),[1] probably due to the fact that, in 3, the lone electron must be equally delocalized over carbons 1 and 3. In support of this argument, the ^{13}C coupling constant of 3 with carbons 1 and 3 (Figure 1a) is much smaller (17.6 G)[3] than that of the α-carbon in perchlorobenzyl (59.3 G). The fact that the ^{13}C coupling constant of radical 3 is not even half the value of that of perchlorobenzyl (59.3/2 = 29.65 G) can be traced to the planarity of the indenyl ring, which allows greater delocalization of the lone electron also into the aromatic ring. It must be pointed out that benzyl radical presents a tilting angle between the plane of the dichloromethylene group and the phenyl ring of about 60°, preventing effective delocalization of the lone electron into the ring. Lande's g value for radical 3 is rather high (2.0065 ± 0.0003), falling in between those of the perchlorobenzyl (2.0072 ± 0.0003)[1] and perchlorodiphenylmethyl (2.0055 ± 0.0003)[4] radicals; this value indicates significant spin-orbit coupling with the chlorines.

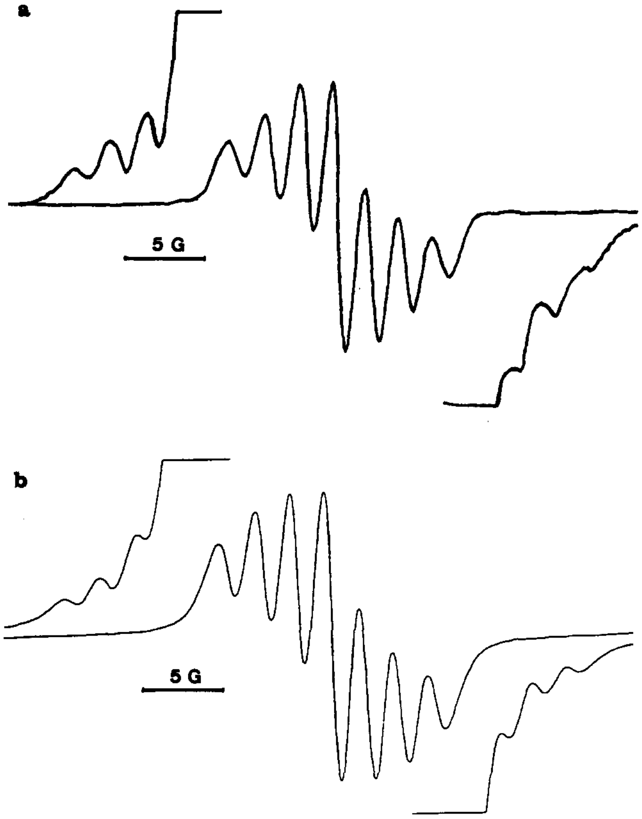


Figure 1. (a) ESR spectrum of perchloro-1-indenyl radical (3). (b) Computer simulated spectrum of 3.

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[1] Olivella, S.; Ballester, M.; Castañer, J. *Tetrahedron Lett.* 1974, 587.

[2] Livingstone, R.; Zeldes, H.; Conardi, M. S. *J. Am. Chem. Soc.* 1979, *101*, 4312.

[3] Calculated by computer simulation (Figure 1b).

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Table I

temp (°C)	$1/T \times 10^3$ (K)	spins ($\times 10^{-16}$)	mol ($\times 10^8$)	K	$\log K$
71	2.907	0.8495	1.410	7.011×10^{-6}	−5.154
81	2.825	1.462	2.427	2.079×10^{-5}	−4.682
101	2.674	3.360	5.579	1.102×10^{-4}	−3.958
111	2.604	5.217	8.662	2.663×10^{-4}	−3.574
120	2.545	6.862	11.393	4.619×10^{-4}	−3.335
130	2.481	8.666	14.388	7.396×10^{-4}	−3.132
141	2.415	10.494	17.423	1.086×10^{-3}	−2.964

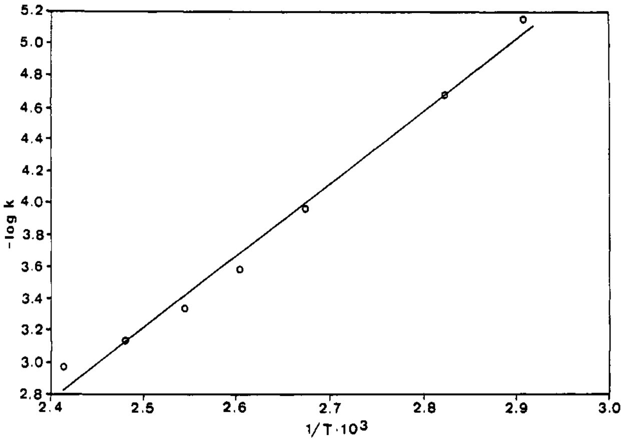

Figure 2. Least-squares regression plot of $-\log K$ versus $1/T$.

Dissociation Energy Calculation. Quantitative measurements of the intensity of the ESR signal by double integration (using DPPH as standard), in the range 71–141 °C,[5] afforded the data contained in Table I, column 3, from which a set of log K values for the dissociation reaction were calculated (column 6). A least-squares linear regression of $-\log K$ versus $1/T$ using the van't Hoff equation with calories and mole fraction as units results in a value of $\Delta H = 20.83$ kcal·mol^{-1} with a correlation coefficient $r = 0.994$ (Figure 2).

$$-\log K = \frac{\Delta H}{2.303\mathrm{R}}(1/T) + C$$

This low value for the dissociation energy can be rationalized in terms of the high resonance stabilization of the planar perchloro-1-indenyl radical (**3**) and the frontal steric strain of the dimer (**2**) which results in its destabilization. These concepts have previously been postulated by Leroy et al.[6] for the dissociation of polysubstituted ethanes. In fact, the dissociation energy value of 20.83 kcal·mol^{-1} for the dimer **2** is similar to values found for hexacyanoethane (22.00 kcal·mol^{-1})[6] and 1,1,2,2-tetrakis(2,6-dimethylphenyl)ethane (22.00 ± 0.55 kcal·mol^{-1}).[7]

Experimental Section

Equipment. The IR, ESR, and mass spectra were recorded on Perkin-Elmer Model 682, Varian Model E-109E (equipped with a Varian E-232 dual sample reactangular cavity and a Varian E-257 variable-temperature controller), and V. G. Model TS-250 spectrometers, respectively. The ESR computer simulation was performed with a Varian E-935 data acquisition system, using a modified version of its software pack.

Perchlorobis(1-indenyl) (2). Iron pentacarbonyl (0.063 g; 0.320 mmol) was added to a degassed solution of perchloroindene (**1**) (0.250 g; 0.638 mmol) in benzene (50 mL) under N_2. The solution was refluxed (5 min) and evaporated to dryness in vacuo. The resulting solid was extracted with $CHCl_3$ and recrystallized from hexane yielding perchlorobis(1-indenyl) (**2**) (0.177 g; 77.8%) mp 206–8 °C dec: IR (KBr) 1583 (s), 1360 (s), 1300 (s), 1210 (s), 1176 (s), 1138 (m), 800 (m), 770 (m), 720 (m), 640 (m), 630 (m), 585 (m), 566 (m), 500 (m) cm^{-1}; MS (all ^{35}Cl)[8] (calcd for $C_{18}Cl_{14}$, 706): *m/e* (relative intensity) 706 (0.3; M$^+$), 636 (3.5; M$^+$ − 2Cl), 566 (3.1; M$^+$ − 4Cl), 496 (1.6; M$^+$ − 6Cl), 353 (100; M$^+$/2), 318 (22.4; M$^+$/2 − Cl), 283 (35, M$^+$/2 − 2Cl), 248 (2.2, M$^+$/2 − 3Cl), 213 (12, M$^+$/2 − 4Cl). Anal. Calcd for $C_{18}Cl_{14}$: C, 30.3; H, 0.0; Cl, 69.7. Found: C, 30.5; H, 0.1; Cl, 69.7%.

Perchloro-1-indenyl Radical (3). (a) By Thermal Dissociation of Perchlorobis(1-indenyl) (2). A carefully degassed mixture of perchlorobis(1-indenyl) (**2**) and 1,2,3-trichlorobenzene (~5:100) was heated in the cavity of an ESR spectrometer. An ESR signal began to appear around 70 °C, which increased with temperature. A strong stable spectrum was recorded at 150 °C (Figure 1a):[5] *G*, 2.0065 ± 0.0003; seven lines with ^{13}C satellites. Computer simulation (Figure 1b): 7 lines with 1:2:3:4:3:2:1 relative intensities; line width 1.2 G; Cl coupling constant 2.1 G; ^{13}C coupling constant 17.6 G.

(b) By Thermal Dissociation of Perchloroindene (1). The preceding thermal reaction was repeated with perchloroindene (**1**) instead of diindene (**3**). An ESR signal begins to appear around 190 °C, which also increases with temperature. A strong stable spectrum, identical to that described in the preceding paragraph, was recorded at 210 °C.

Quantitative ESR Measurements. Perchlorobis(1-indenyl) (**2**; 3.80 mg, 5.33×10^{-6} mol) was carefully mixed with 1,2,3-trichlorobenzene (0.100 g), poured into an ESR quartz tube, and heated in the cavity of an ESR spectrometer. The resulting data are given in Table I. A solution of DPPH in the same solvent was used as quantitative standard in the same temperature range.

Acknowledgment. This investigation was supported by the DGICYT of MEC, Project no. PB87-0388.

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(4) Ballester, M.; Riera, J.; Castañer, J.; Badía, C.; Monsó, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 2215.

(5) It has been verified that carefully degassed solutions of DPPH in 1,2,3-trichlorobenzene are sufficiently stable over short periods, thus allowing the quantitative ESR measurements. At temperatures over 145 °C, slow irreversible side reactions of radical **3** are observed.

(6) Leroy, G.; Sana, M.; Wilante, C. *J. Mol. Struct.* **1989**, *198*, 159.

(7) Fleurke, K. H. Diarylmethyl Radicals and Symmetrical Tetraarylethanes. Doctoral Thesis; Amsterdam University; Amsterdam (Netherlands), 1963.

(8) All of the peak clusters present isotopic distributions which are in agreement with their number of chlorines. Doubly charged clusters corresponding to the principal fragment ions are also detected.