Reaction of Iron Pentacarbonyl with Perchlorocyclopentadiene

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Iron pentacarbonyl undergoes a facile reaction with perchlorocyclopentadiene \( \text{C}_5\text{Cl}_5 \) (I) giving carbonyl substituted polymer \( \text{[C}_5\text{Cl}_5\text{CO}]_n \) (n = 17) (II), \( \text{C}_10\text{Cl}_{10} \) (III) and \( \text{FeCl}_2 \). Nickel tetracarbonyl, but not \( \text{M(CO)}_4 \) (M = Cr, Mo or W), reacts with I to produce II, III and \( \text{NiCl}_2 \). Spectral data are presented in support of the structures of the compounds isolated.

Under similar experimental conditions nickel tetracarbonyl, gave \( \text{[C}_5\text{Cl}_5\text{CO}]_n \), \( \text{C}_{10}\text{Cl}_{10} \) and \( \text{NiCl}_2 \). Sixth group metal carbonyls, \( \text{M(CO)}_4 \) (M = Cr, Mo, W) did not react with \( \text{C}_5\text{Cl}_5 \) under similar experimental conditions; a drastic condition, however, led to the decomposition of metal carbonyls.

**Results and Discussion**

Iron pentacarbonyl reacts with perchlorocyclopentadiene (I) in refluxing benzene readily with the evolution of carbon monoxide (identified by its IR spectrum), precipitation of ferrous chloride and formation of a polymeric compound \( \text{[C}_5\text{Cl}_5\text{CO}]_n \) (n = 17) (II) and bis (pentachlorocyclopentadienyl) (III). The compounds were characterised by their elemental analyses, and IR and mass spectral data. The IR spectrum of II shows characteristic ring modes and \( \nu \text{ C-Cl} \) stretching vibrations at 802 vs and 705 s. A distinguishing feature of the spectrum is the presence of a band at 1560 cm\(^{-1}\) which has been assigned to \( \nu \text{(C=C)} \). The occurrence of a medium intensity band at 1720 with a shoulder at 1745 cm\(^{-1}\) indicates the presence of a CO group with a \( \nu \text{ C-O} \) bond order of two. Additional support for this formulation has been obtained from mass spectral data. A careful perusal of mass spectrum of the compound revealed the presence of a weak peak at \( m/e \ 231 \) (4.8\%) which became weaker by raising the temperature of the ion source maintaining the ionising radiation at 70eV. This peak has been assigned to \( \text{[C}_5\text{Cl}_5\text{CO}]^+ \) fragment. A characteristic feature of the spectrum is the presence of a relatively strong peak at \( m/e \ 28 \) (15.7\%) due to \( \text{CO}^+ \) fragment. Besides these, the peaks at \( m/e \ 203 \) (14.8\%), 167 (13.4\%), 141 (13.8\%), 130 (21.3\%), 95 (27.8\%), 60 (15.8\%), 37 (3.1\%) and 35 (9.8\%) have been identified (Scheme 1).

**Materials and Methods**

All reactions and other manipulations were done under dry nitrogen or argon. IR spectra were recorded on a Perkin-Elmer model 125 grating spectrophotometer and the mass spectra on a CH5 Varian MAT mass spectrometer at 70eV ionizing radiation.

**Reaction of Fe(CO)\(_5\) with perchlorocyclopentadiene (C\(_5\)Cl\(_5\))** — In a typical reaction, a mixture of C\(_5\)Cl\(_5\) (1 mmol) and iron pentacarbonyl (3 mmol) was stirred at room temperature for 15 min., followed by the addition of benzene. The mixture was refluxed at 83–84\°C for 1 hr, filtered, the filtrate concentrated, and n-pentane added to give a brown product. This was dissolved in dichloromethane, filtered and the filtrate concentrated under a constant flow of argon to give deep red-brown shining flakes of a polymeric compound \( \text{[C}_5\text{Cl}_5\text{CO}]_n \) in \(~40\%\) yield; mol. wt. 3910 \((n = 17)\) (Found : C, 31.31; Cl, 61.72. \( \text{C}_5\text{Cl}_5\text{O} \) requires C, 31.35; Cl, 61.69\%); IR: 1592 vs, 1560 m, 1245 vs, 1175 m, 1152 m, 965 m, 956 m, 675 s, 535 w (ring modes); \( \nu \text{ C-Cl} \) stretching vibrations at 802 vs and 705 s. A distinguishing feature of the spectrum is the presence of a band at 1560 cm\(^{-1}\) which has been assigned to \( \nu \text{(C=C)} \). The occurrence of a medium intensity band at 1720 with a shoulder at 1745 cm\(^{-1}\) indicates the presence of a CO group with a \( \nu \text{ C-O} \) bond order of two. Additional support for this formulation has been obtained from mass spectral data. A careful perusal of mass spectrum of the compound revealed the presence of a weak peak at \( m/e \ 231 \) (4.8\%) which became weaker by raising the temperature of the ion source maintaining the ionising radiation at 70eV. This peak has been assigned to \( \text{[C}_5\text{Cl}_5\text{CO}]^+ \) fragment. A characteristic feature of the spectrum is the presence of a relatively strong peak at \( m/e \ 28 \) (15.7\%) due to \( \text{CO}^+ \) fragment. Besides these, the peaks at \( m/e \ 203 \) (14.8\%), 167 (13.4\%), 141 (13.8\%), 130 (21.3\%), 95 (27.8\%), 60 (15.8\%), 37 (3.1\%) and 35 (9.8\%) have been identified (Scheme 1).
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References