$C^{18}O$ Exchange Studies on $Mn(CO)_5X$ Systems ($X = Cl$ or Br)

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ON the basis of radiocarbon monoxide exchange studies carried out on compounds of the type $Mn(CO)_5X$, ($X = Cl$, Br, or I)[1,2] Basolo and Wojcicki[1] suggested that the four equatorial carbon monoxide groups exchanged at a much faster rate than the axial CO group. This observation led us to consider the possibility of synthesising molecules of the type $Mn(C^{18}O)_4(C^{16}O)X$ and $Mn(C^{16}O)_4(C^{18}O)X$ to allow a more accurate determination of the force constants (k_1, k_2, k_c, k_c', and k_t) and to provide a useful method of checking the Kraihanzel and Cotton model.[3]

$C^{18}O$ was prepared from $H_2{}^{18}O$ (97·7%) by the water-gas method. The *minimum* $C^{18}O$ content, determined by both mass-spectrometric and infrared-spectral methods, was found to be 86%. Exchange studies were carried out on the chloride and bromide following essentially the same procedure as that adopted by Basolo and Wojcicki.[1,4]

Figures 1—4 show the variations in the C–O stretching region during a typical exchange experiment. This variation was the same in a number of experiments carried out in either chloroform or toluene at 20° and 50°. The results at both temperatures were similar although the overall rate was considerably faster at 50°.

The spectra were analysed by calculating the frequencies of all possible substituted species from the force constants given by Cotton.[5] The most significant features to emerge from the calculation were that a frequency at 1958 cm.$^{-1}$ was common and specific to all species containing an axial $C^{18}O$ group and that the band at 2135 cm.$^{-1}$ diminishes in intensity only on substitution of equatorial groups. No new bands were observed between 2000 and 1958 cm.$^{-1}$ (Figures 1—4). This indicates that the initial assignment of the 2000 cm.$^{-1}$ band to the axial CO vibration is correct and that the coupling between the axial and equatorial groups is not large. By following the bands at 2135 and 1958 cm.$^{-1}$, approximate rate constants were calculated and it would appear that the rates of radial and equatorial substitution are of the same order under all the conditions we have used.

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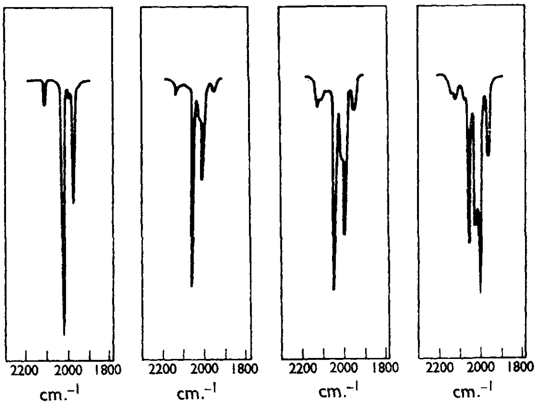

1 2 3 4

FIGURES

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