$(TRI)^{2+}$ does not racemize. This is probably a fair assumption in light of the extreme inertness to dissociation and racemization found for this material.

The $Ni(TRI)_2^{2+}$ produced from partially resolved $Ni(TRI)^{2+}$ has no observable rotation. Therefore, the $Ni(TRI)_2^{2+}$ exists in only the *meso* form, and the reaction shown in Figure 4 proceeds stereospecifically (by path 1).

Efforts to prepare $Ni(TRI)(5\text{-}Cl\text{-}TRI)(NO_3)_2$ by the reaction of resolved $Ni(TRI)^{2+}$ with the bis anhydro trimer of 2-amino-5-chlorobenzaldehyde under numerous conditions have thus far failed indicating again the less reactive properties of the chloro derivative.[17] On the other hand, the more reactive $(oab)_3$ does rearrange in the presence of $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2(C_2H_5OH)$ or $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2(H_2O)$ to give $Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2\cdot H_2O$. Evidence for the composition of this compound has been obtained primarily from elemental analyses and infrared spectra. In Table VI several infrared absorption bands for $Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2\cdot 2H_2O$ are listed and compared with corresponding infrared absorption bands for $Ni(TRI)(NO_3)_2(H_2O)$ and $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2(H_2O)$. It can be seen that $Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2\cdot 2H_2O$ has bands characteristic of both chloro- and unsubstituted trimeric condensates. The magnetic moment, absorption spectrum, and physical and chemical properties for this material suggest a structure analogous to $Ni(TRI)_2(NO_3)_2(H_2O)$ (see Tables II and III) which probably exists in the isomeric form with its benzene rings in a staggered conformation.

TABLE VI

INFRARED SPECTRA[a] OF THE NICKEL(II) COMPLEXES CONTAINING CHLORO- AND UNSUBSTITUTED TRIMERIC CONDENSATES OF *o*-AMINOBENZALDEHYDE

| Assignment | $Ni(TRI)(NO_3)_2\cdot H_2O$ | $Ni(5\text{-}Cl\text{-}TRI)(TRI)(NO_3)_2\cdot 2H_2O$ | $Ni(5\text{-}Cl\text{-}TRI)(NO_3)_2\cdot H_2O$ |
|---|---|---|---|
| $C_6$ ring I | 1620 vs | 1617 vs | 1621 vs |
| $C_6$ ring II | 1592 s | 1590 m | 1590 m |
| C═N str | 1569 s | 1565 m | . . . |
| C═N str | . . . | 1558 m | 1560 m |
| $C_6$ ring III | 1488 m | 1484 s | 1484 s |
| $C_6$ ring IV | 1441 m | 1441 m | 1443 m |
| C—H def | . . . | 881 w | 881 m |
| C—H def | . . . | 833 s | 833 vs |
| C—H def | 769 vs | 781 s | . . . |
| C—Cl str | . . . | 717 m | 720 s |

[a] Abbreviations used: b, broad; s, strong; m, medium; w, weak; v, very.

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[17] Regardless of the manner in which the chloro-Schiff base had coordinated to the $Ni(TRI)^{2+}$, the resulting product would have been asymmetric and if racemization had not occurred, the product would have had an observable rotation.

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# Notes

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## Isotopic Exchange Reactions of Carbon Monoxide with Rhenium Pentacarbonyl Halides

BY G. CETINI, O. GAMBINO, G. A. VAGLIO, AND R. P. FERRARI

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A considerable number of studies on the behavior of metal carbonyls in exchange and substitution reactions have appeared in recent years. These have been directed to the collection of data on compound reactivity *via* such parameters as coordinator element type, degree of substitution of CO groups, and so on. Some excellent papers on this subject have already appeared.[1,2]

Our previous studies were concerned with the exchange reaction behavior of metal carbonyls containing elements of groups VI and VIII of the periodic table, in particular Cr, Mo, and W carbonyls[3-5] and Fe, Ru, and Os tricarbonyls.[6,7] The present paper reports CO isotopic exchange reactions with rhenium pentacarbonyl halides; data dealing with similar reactions involving technetium pentacarbonyl halides are being prepared for publication in a separate work.

Previous studies carried out with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ had met with little success. When light was excluded, the exchange rate was very slow and the behavior of photochemical reactions could not be accurately determined.

Our present results are compared with already published data dealing with exchange[8,9] and substitution[10] reactions involving compounds of the $Mn(CO)_5X$ type

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TABLE I

ISOTOPIC EXCHANGE REACTIONS OF CO WITH $Re(CO)_5X$

| $[Re(CO)_5X]$, m*M* | $[CO]_{tot}$,[a] m*M* | Temp, °C | $10^5 k_{obsd}$[b] | Solvent |
|---|---|---|---|---|
| | | $Re(CO)_5Cl$ | | |
| 0.741 | 79.0 | 35.0 | 0.80 | Toluene |
| 1.23 | 90.2 | 35.0 | 0.81 | Toluene |
| 0.525 | 82.2 | 42.0 | 2.26 | Toluene |
| 1.05 | 8.6 | 49.8 | 7.3 | Toluene |
| 1.02 | 25.3 | 49.8 | 7.2 | Toluene |
| 1.46 | 84.4 | 49.8 | 7.0 | Toluene |
| 0.250 | 1.41 | 42.0 | 9.4 | Toluene |
| 0.170 | 1.59 | 42.0 | 5.6 | Toluene |
| 0.102 | 1.57 | 42.0 | 3.2 | Toluene |
| 0.105 | 0.55 | 42.0 | 7.0 | Toluene |
| | | $Re(CO)_5Br$ | | |
| 1.01 | 84.0 | 40.0 | 0.34 | Toluene |
| 1.22 | 80.0 | 40.0 | 0.32 | Toluene |
| 0.80 | 8.5 | 50.0 | 1.55 | Toluene |
| 1.26 | 80.0 | 50.0 | 1.61 | Toluene |
| 0.194 | 1.34 | 50.0 | 1.94 | Toluene |
| 0.101 | 1.60 | 50.0 | 1.77 | Toluene |
| 1.01 | 84.0 | 60.0 | 6.8 | Toluene |
| 1.22 | 80.0 | 60.0 | 6.7 | Toluene |
| 0.130 | 89.0 | 60.0 | 6.4 | Toluene |
| 0.55 | 1670 | 60.0 | 7.1 | Toluene |
| 0.77 | 5500 | 60.0 | 6.9 | Toluene |
| 0.420 | 97 | 40.1 | 0.95 | *n*-Heptane |
| 0.400 | 91.9 | 50.1 | 4.1 | *n*-Heptane |
| 0.400 | 9.6 | 50.1 | 4.1 | *n*-Heptane |
| 0.400 | 90.9 | 59.8 | 15.5 | *n*-Heptane |
| 0.491 | 85 | 60.0 | 5.0 | Chloroform |
| | | $Re(CO)_5I$ | | |
| 1.03 | 90.8 | 50.7 | 0.199 | Toluene |
| 1.03 | 8.1 | 50.7 | 0.196 | Toluene |
| 0.217 | 1.52 | 50.7 | 0.30 | Toluene |
| 1.68 | 92.4 | 57.6 | 0.58 | Toluene |
| 1.15 | 94 | 64.3 | 1.56 | Toluene |

[a] Total concentration of CO calculated as all was in solution. [b] First-order rate constant, calculated assuming a first-order law with respect to the complex.

(X = Cl, Br, I) and substituion reactions with the same rhenium complexes.[11]

Preliminary CO isotopic exchange experiments with $Re(CO)_5X$ (X = Cl, Br, I) in toluene and other solvents have shown, in agreement with recently reported data,[12] that the five carbonyl groups are kinetically equivalent. The results collected in Table I show that exchange reactions follow a first-order law with respect to the complex, irrespective of CO concentration values, provided these are not less than 8–10 m*M*. A dissociative mechanism is thus involved, in which the slow step consists of the rupture of an Re–CO bond.

Table I also shows that, where CO concentration is of the order of 1 m*M*, $k_{obsd}$ values (a) are higher than those encountered in the presence of 8–10 m*M* CO concentrations, (b) decrease with decreasing complex concentration values, and (c) increase with decreases in CO concentration (complex concentration values being equal). These aspects of $k_{obsd}$ behavior were evident for all three complexes, though the clearest evidence was obtained with $Re(CO)_5Cl$. They are explicable on the assumption that, when CO concentration is low, a dimer is formed

$$2Re(CO)_5X \rightleftharpoons [Re(CO)_4X]_2 + 2CO$$

followed by the dimer exchange.

It should be noted that the presence of this dimer has not been shown experimentally. However, experiments, run under similar conditions, on the dimer itself have shown that its exchange rate is much higher than that of the monomer. From these facts, it can safely be suggested that a small quantity of dimer is formed and that this quantity decreases with the monomer concentration and increases with decreases in CO concentration, according to the previous state of equilibrium. The contribution that this formation and exchange of a dimer makes to the exchange reaction as a whole will depend on the concentration of the dimer. Therefore, at the lower concentrations of CO one could take into account a reaction mechanism involving other than the reaction slow step (rupture of the Re–CO bond) and also a stage where $[Re(CO)_4X]_2$ dimer systems take part.

TABLE II

ACTIVATION PARAMETERS FOR SUBSTITUTION REACTIONS OF $Mn(CO)_5X$[a] AND EXCHANGE AND SUBSTITUTION[b] REACTIONS OF $Re(CO)_5X$

| | Substitution $E_a$, kcal mol$^{-1}$ | Exchange $E_a$, kcal mol$^{-1}$ | Substitution $\Delta S^{\ddagger}$, eu | Exchange $\Delta S^{\ddagger}$, eu | Solvent[c] |
|---|---|---|---|---|---|
| $Mn(CO)_5Cl$ | 27.5 ± 0.4 | | 15.7 | | Chloroform |
| $Mn(CO)_5Br$ | 29.8 ± 0.4 | | 18.9 | | Chloroform |
| $Mn(CO)_5I$ | 32.2 ± 0.4 | | 20.7 | | Chloroform |
| $Mn(CO)_5Br$ | 30.9 | | 22.1 | | Nitrobenzene |
| | Substitution $\Delta H^{\ddagger}$, kcal mol$^{-1}$ | | | | |
| $Re(CO)_5Cl$ | 30.5 ± 0.1 | 29.2 ± 0.7 | 17.5 ± 0.3 | 10.6 ± 2.4 | Toluene |
| $Re(CO)_5Br$ | 29.45 ± 1.8 | 31.5 ± 0.2 | 10.7 ± 5.4 | 14.8 ± 0.9 | Toluene |
| $Re(CO)_5I$ | 27.9 ± 5.6 | 33.0 ± 0.3 | 2.2 ± 16.8 | 15.2 ± 1.2 | Toluene |
| $Re(CO)_5Br$ | | 29.4 ± 0.1 | | 10.2 ± 0.6 | *n*-Heptane |

[a] Values from ref 10. [b] Values in carbon tetrachloride from ref 11. [c] Solvents used in substitution reactions of $Mn(CO)_5X$ and in exchange reactions of $Re(CO)_5X$.

As already reported for $Mn(CO)_5X$, the specific rate constants follow the order Cl > Br > I. This is in agreement with the increase in order of the Re–C bond from the chlorine to the iodine derivative and is deducible from the shift of the highest C–O stretching frequencies.

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[11] F. Zingales, M. Graziani, F. Faraone, and U. Belluco, *Inorg. Chim. Acta*, **1**, 172 (1967).

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The effect produced by the solvent was studied on $Re(CO)_5Br$. Specific rate constants decreased with increasing solvent dielectric constant values; $E_a$ values varied in the inverse order.

These results can be explained by suggesting a decrease in polarity in going from $Re(CO)_5X$ to the activated complex. Similar behavior has been reported for dissociative substitution reactions involving $Mn(CO)_5X$.[4]

Table II gives the energy and entropy of activation values and these are typical of the mechanism suggested. $E_a$ values are compared with those obtained in the (also dissociative) substitution reactions of $Re(CO)_5X$ and $Mn(CO)_5X$. It will be noted that our $Re(CO)_5X$ exchange values vary inversely with those reported by other writers[11] for substitution reactions with these complexes but follow the same order (*i.e.*, $Cl < Br < I$) as those reported for $Mn(CO)_5X$ substitution reactions.[10]

Table II also shows lower $E_a$ values for the manganese complex, but it must be pointed out that direct comparison is, in fact, unfeasible since the reactions were carried out in different solvents. However, reduction of the solvent dielectric constant is known to lead for these compounds to decreased $E_a$ values and it may thus be deduced that the values for $Mn(CO)_5X$, as reported for chloroform, would have been lower had toluene been used and that the difference already apparent in Table II would in fact have been greater.

We can, therefore, claim lower reactivity for rhenium as opposed to manganese derivatives. This can be attributed to the greater ability of rhenium to form a $\pi$ bond by the coupling of $d_\pi$ electrons with carbon antibonding orbitals, a phenomenon generally observed in going from 3d to 5d metal complexes. For this reason, greater energy is needed to obtain the rhenium five-coordinated complex.

### Experimental Section

Already reported techniques and treatment of data[13] were used for the exchange reactions.

In the case of high CO pressure reactions, we used a steel line equipped with a pressure gauge calibrated up to 25 atm. For reaction containers, we employed small steel bottles controlled by a needle valve. These were connected to the line by means of metal joints.

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[13] G. Cetini, O. Gambino, P. L. Stanghellini, and G. A. Vaglio, *Inorg. Chem.*, **6**, 1225 (1967).

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## Magnetic Susceptibility of Cubic Uranium Tungsten Bronzes between 4.2 and 560°K[1]

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The magnetic susceptibility of three uranium tungsten bronzes $U_xWO_3$ ($x$ = 0.08, 0.10, 0.12) and of a mixed uranium–thorium tungsten bronze $U_{0.033}Th_{0.067}WO_3$ has been measured between 4.2 and 560°K. The bronzes were prepared as powders by allowing $UO_2$ ($ThO_2$), $WO_2$, and $WO_3$ to react in the proper molar ratio. The carefully ground reagents were enclosed in an evacuated, sealed silica capsule and heated for at least 100 hr at 1000° from which temperature they were rapidly cooled. Reaction products were studied by X-ray powder diffraction photography for homogeneity. The lattice parameters of the bronzes are listed in Table I.

TABLE I

CRYSTALLOGRAPHIC AND MAGNETIC DATA OF CUBIC URANIUM TUNGSTEN BRONZES

| M in $M_xWO_3$ | Lattice parameter $a_0$, Å | Δ distance U–U, Å | $10^6\chi_g$ at 4.2°K, cgsu | $\mu_{eff}$ of U,[a] $\mu_B$ |
|---|---|---|---|---|
| $U_{0.08}$ | $3.805_2$ | 9.10 | 0.008 | $3.1_2$ |
| $U_{0.10}$ | $3.809_6$ | 8.35 | 0.006 | $3.1_0$ |
| $U_{0.12}$ | $3.813_3$ | 7.75 | 0.005 | $3.1_1$ |
| $U_{0.033}Th_{0.067}$ | $3.825_5$ | 11.60 | 0.006 | $3.1_2$ |

[a] In the computation of $\mu_{eff}$ of uranium, corrections were made by use of experimentally determined $\chi$ values of $Th_xWO_3$ ($x$ = 0.08, 0.10, 0.12).

Magnetic susceptibility measurements were made by the Gouy method. The magnetic instrument consisted of a RH Cahn electrobalance with vacuum attachment, a 6-in. Varian electromagnet carrying tapered pole caps, and a Moseley X-Y recorder. The field was calibrated with $CoHg(SCN)_4$;[2] between 1 and 14 kG, field calibration was reproducible better than 0.2%. Temperature readings were accurate to ±1°. Force measurements were made at various temperatures and fields using ~4-g heavy, ~25-cm long specimens. A very slight field dependence of the susceptibilities was corrected for by extrapolating the $\chi$ values to zero reciprocal field.

Figure 1 shows $1/\chi$–$T$ plots for the four compounds investigated. It can be seen that all curves are linear above roughly 60°K, and their linear portions extrapolate to a common value of $-170 \pm 5$°K. At lower temperatures, susceptibilities pass through a maximum at 30°K and then drop rapidly toward zero. Table I lists the $\chi_g$ values of the various uranium bronzes observed at 4.2°K. Field dependence of the susceptibility maxima was not observed.

Data suggest that antiferromagnetic exchange interactions are the cause of the $\chi$–$T$ behavior of $U_xWO_3$ (Curie–Weiss type, $\Theta = -170 \pm 5°$). This permits evaluation of the effective moment of uranium on the basis of $\mu_{eff} = 2.84[\chi_{U^{4+}}(T - \Theta)]^{1/2}$. Table I lists the moments of uranium for each of the bronzes as calculated from this equation.

There are three possible mechanisms to be considered to explain the presence of exchange interactions in cubic uranium tungsten bronzes: the first involves direct U–U interactions; the second, coupling by bridging through an intervening oxygen atom (U–O–U superexchange); and the third, indirect coupling

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[1] This work is dedicated to Professor Dr. W. Rüdorff, University of Tübingen, Germany, in honor of his 60th birthday.

[2] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).