TABLE I

RAMAN FREQUENCIES, IN CM.$^{-1}$, FROM CONCENTRATED AQUEOUS SOLUTIONS OF METAL NITRATES

	C_{2v}, bound nitrate					D_{3h}, free nitrate		
Nitrate	$\nu_4(B_1)$	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(B_2)$ or $\nu_5(B_1)$	$\nu_3(A_1)$	$\nu_3(E')$	$\nu_1(A_1')$	$\nu_4(E')$
Na^+						1410	1052	720
K^+						1400	1055	725
NH_4^+						1400	1052	725
Ag^+		1340				1420	1040	720
Cu^{2+}	1490	1325	1040	810	760	1425	1060	725
Zn^{2+}		1340				1425	1052	720
Hg^{2+}	1465	1320		810	735	1400	1040	720
Ca^{2+}	1450	1360			744	1400	1053	720
Al^{3+}		1340				1420	1048	720
In^{3+}	1510	1315	1040		750	1425	1050	720
Ce^{3+}	1470	1360		830	745	1400	1050	720
Th^{4+}	1536	1322	1039	810	745	1428	1052	717
Polarization	dp	p	p	dp	p/dp	dp	p	dp

TABLE II

RAMAN FREQUENCIES, IN CM.$^{-1}$, FROM CONCENTRATED AQUEOUS SOLUTIONS OF METAL SULFATES

	C_{3v}, bound sulfate				T_d, free sulfate			
Sulfate	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu(M–O)$	$\nu_3(F_2)$	$\nu_1(A_1)$	$\nu_4(F_2)$	$\nu_2(E)$
Na^+					1105	980	625	450
NH_4^+					1120	985	620	460
Tl^+					1100	985	625	452
Cu^{2+}					1100	980	620	450
Zn^{2+}					1112	985	618	455
Cd^{2+}					1105	985	615	451
Mg^{2+}					1120	985	618	455
Al^{3+}					1100	985	625	455
Ga^{3+}					1200	985	600	475
In^{3+}	1125	1000	650	225	1105	980	620	~450[a]

[a] Overlap with an aquo–indium complex line prevented precise determination of the $\nu_2(E)$ frequency from the In^{3+} salt.[3]

TABLE III

RAMAN FREQUENCIES, IN CM.$^{-1}$, FROM CONCENTRATED AQUEOUS SOLUTIONS OF METAL PERCHLORATES

	Point group T_d assignment			
Perchlorate	$\nu_3(F_2)$	$\nu_1(A_1)$	$\nu_4(F_2)$	$\nu_2(E)$
Na^+	1112	942	634	465
Li^+	1120	941	636	468
H^+ (70% $HClO_4$)	1125	933	630	460
Ag^+	1105	929	625	462
Be^{2+}	1130	937	631	464
Mg^{2+}	1130	940	634	467
Ca^{2+}	. . .	942	634	465
Cu^{2+}	1120	940	635	470
Hg^{2+}	1110	938	633	467
Pb^{2+}	1105	937	632	465
Al^{3+}	1120	937	632	465
In^{3+}	1125	935	630	465
La^{3+}	1130	939	634	467
Ce^{3+}	. . .	933	630	462
Th^{4+}	1110	940	633	465

with the various metal ions.[11] The Raman results given in Table I reveal the following order of nitrate deformations: $Th^{4+} > In^{3+} > Cu^{2+} > Hg^{2+} > Ce^{3+} > Ca^{2+} > Zn^{2+}, Al^{3+}, Ag^+ > Na^+, K^+, NH_4^+$.

A more sensitive test of the invariance of the spectra of the sulfate and perchlorate ions is the intercomparison of line intensities. Accordingly, measurements of the molar intensities of the $\nu_1(A_1)$ lines from solutions listed in Tables II and III have been made, but were found to be constant within the possible 6% limit of experimental error.[12] Likewise, no significant change in the relative intensities of the four fundamentals was discovered by intercomparisons in the perchlorate series.[12] Our measurements justify the use of the $\nu_1(A_1)$ line of the perchlorate ion as an internal standard for Raman line intensity measurements under usual aqueous conditions. It is clear that the tetrahedral symmetry of the anion is not appreciably diminished for any of the perchlorates or any of the sulfates with the exception of In^{3+}.

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(11) J. R. Ferraro, *J. Mol. Spectry.*, **4**, 99 (1960).

(12) R. E. Hester, Thesis, Cornell University, 1962.

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Metal Carbonyls. VIII. Kinetics of Carbon Monoxide Exchange with Trichlorobis(triphenylphosphine)carbonylrhodium(III)

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Compounds of the types $[Rh(PR_3)_2COCl]$ and $[Rh(PR_3)_2COCl_3]$ were first prepared by Vallarino[1] and described as being very stable because the compounds do

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(1) L. Vallarino, *J. Chem. Soc.*, 2287 (1957); *J. Inorg. Nucl. Chem.*, **8**, 288 (1958).

TABLE I

RATES OF CO EXCHANGE WITH $[Rh(P(C_6H_5)_3)_2COCl_3]$ IN CHLOROFORM

$[Rh(P(C_6H_5)_3)_2COCl_3]$, *M*	$[CO]$,[a] *M*	Temp., °C.	10^5k, sec.$^{-1}$
0.00305	0.01510	25	3.43
0.00260	0.00794	25	3.63
0.00246	0.00337	25	3.40
0.00258	0.00203	25	3.45
0.00138	0.00370	25	3.28
0.00272	0.00413	35	6.54[b]
0.00275	0.00360	45	14.1[b]
0.00255	0.00392	25	4.15[c]
0.00251	0.00378	25	3.75[d]
0.00272	0.00370	25	13.2[e]

[a] The concentration of CO is expressed as if all the CO in the enclosed system were in solution. [b] This temperature dependence permits an estimate of E_a = 14.3 kcal./mole. [c] Solution also contains 0.00114 *M* $[Rh(P(C_6H_5)_3)_2COCl]$ and 0.374 *M* benzyldimethyl{2-[2-(*p*-1,1,3,3-tetramethylbutylphenoxy)ethoxy]ethyl}ammonium chloride. [d] Solution also contains 0.374 *M* benzyldimethyl{2-[2-(*p*-1,1,3,3-tetramethylbutylphenoxy)ethoxy]ethyl}ammonium chloride. [e] The solvent is tetrahydrofuran.

not react on prolonged treatment with different reagents. However, Gray and Wojcicki[2] found that the rhodium(I) compound, $[Rh(P(C_6H_5)_3)_2COCl]$, undergoes exchange reactions very rapidly; it is thus very labile as well as very stable. Therefore, it was decided to investigate the analogous rhodium(III) system, $[Rh(P(C_6H_5)_3)_2COCl_3]$. This paper reports the results of a kinetic study of the exchange of carbon monoxide with the rhodium(III) compound.

A comparison of the rate of carbon monoxide exchange for the rhodium(I) and rhodium(III) systems is of interest because this then can be compared to the nature of the rhodium–carbon bond, as deduced from the infrared spectra of the compounds. The infrared absorption band corresponding to C–O stretch occurs at 1981 cm.$^{-1}$ for the rhodium(I) compound and at 2108 cm.$^{-1}$ for the rhodium(III) compound. This suggests that the degree of π-bonding (back-donation of electron density from rhodium to carbon monoxide, Rh=CO) is greater for the rhodium(I) compound than for the rhodium(III) compound. Although the rhodium–carbon bond strength is presumably greater in the rhodium(I) system, it undergoes carbon monoxide exchange extremely rapidly compared to the rhodium(III) system. This is perhaps due to a different mechanism of exchange for the four- and the six-coordinated compounds. The square-planar rhodium(I) compound undergoes exchange by a low energy displacement (SN2) process,[3a] this being fairly general for substitution reactions in square complexes.[3b] Data in Table I, however, show that for the octahedral rhodium(III) compound, exchange takes place by a dissociation (SN1) process (1). The rate of exchange does not depend on the concentration of carbon monoxide.

$$[Rh(P(C_6H_5)_3)_2COCl_3] \rightleftharpoons [Rh(P(C_6H_5)_3)_2Cl_3] + CO \quad (1)$$

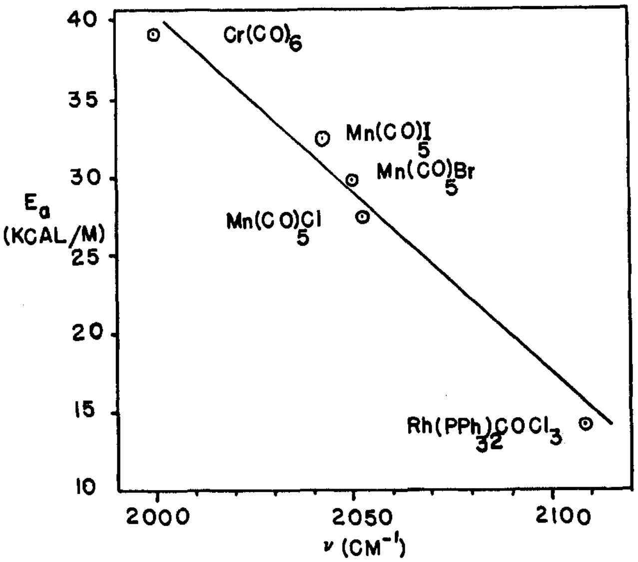

Fig. 1.—The activation energies for the replacement of carbon monoxide from metal carbonyls *vs.* the C–O stretching frequencies. The values of E_a for $Mn(CO)_5X$ are from ref. 6 and for $Cr(CO)_6$ from ref. 7. The frequency values for $Mn(CO)_5X$ are for the antisymmetric stretch for the four CO groups in the plane and are from M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962).

Alternative mechanisms are possible for this exchange but these seem less likely than that represented by (1). For example, the rate-determining step might be the dissociation of a chloride ion followed by the rapid addition of carbon monoxide to the five-coordinated cationic species. This would result in the chloride ion and carbon monoxide competing for the active intermediate, and the rate of exchange may depend on the concentration of carbon monoxide. Such is not the case as shown by the data in Table I. Likewise this mechanism suggests that the rate of exchange may be retarded with added chloride ion, but instead it is found that the addition of R_4NCl slightly increases the rate of exchange. If the rate of addition of carbon monoxide to the reactive intermediate, $[Rh(P(C_6H_5)_3)_2COCl_2]^+$, were very much faster than the rate of return of chloride ion, the rate of reaction would not depend on the concentration of carbon monoxide nor would it be retarded by added chloride ion. This is possible but seems somewhat unlikely because none of the dicarbonyl species can be detected even in the presence of excess carbon monoxide. One other complication is that the failure to observe a chloride ion retardation may be due to a positive salt effect. This would require that the decrease in rate due to chloride ion be exactly compensated for by an increase in rate due to the salt effect. Such opposing effects would be most fortuitous but of course not impossible. Unfortunately this quaternary ammonium nitrate is not soluble in chloroform and the salt effect has not been determined.

Similarly a five-coordinated species may result from the dissociation of triphenylphosphine. Again this may result in the rate of exchange depending on the

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[2] H. B. Gray and A. Wojcicki, *Proc. Chem. Soc.*, 358 (1960).

[3] (a) A. Wojcicki and H. B. Gray, Abstracts, 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 32M; (b) F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 392 (1962).

concentration of carbon monoxide. An attempt to investigate the effect of added triphenylphosphine on the rate of exchange was not successful. Under these conditions the rhodium(III) compound is readily reduced to the rhodium(I) compound, as shown by the infrared spectrum of the solution. This is a surprising observation, deserving further study, because Vallarino reports that the rhodium(III) compound is not reduced by reducing agents such as hypophosphorous acid and magnesium or zinc powder in ethanol. This may just be due to the insolubility of the rhodium(III) compound in ethanol.

These rhodium(I) and rhodium(III) compounds, like the complexes of platinum(II) and platinum(IV), are low-spin d^8 square-planar and low-spin d^6 octahedral systems, respectively. Substitution reactions of some platinum(IV) complexes are catalyzed by platinum(II) by a two-electron bridged activated complex mechanism.[4] It was found that for the particular system under investigation, rhodium(I) has only a very small effect on the rate of reaction of rhodium(III). This is not too surprising because molecular models show it would be difficult to form the chloro-bridged activated complexes due to the large size of the triphenylphosphine groups. For systems where the bridged complex can be formed, catalysis of rhodium(III) reactions has been observed.[5] Finally, the rate of carbon monoxide exchange in the better coordinating solvent tetrahydrofuran is only approximately four times faster than it is in chloroform. This suggests a general solvent effect rather than a specific solvent displacement type process.

In addition to the compound discussed here, the replacement of carbon monoxide from six-coordinated metal carbonyls has been reported for $Mn(CO)_5X$ (where $X = Cl^-, Br^-, I^-$)[6] and for $Cr(CO)_6$.[7] In every case the reaction proceeds by a dissociation mechanism. It would therefore be of interest to compare the activation energies for these reactions with the metal–carbon bond strengths for the different compounds. The bond strengths are not known, but the infrared spectra give the C–O stretching frequencies, which provide an indication of the metal–carbon bond order. The higher the frequency of the C–O absorption, the lower the metal–carbon bond order. A plot of the activation energies for the replacement of carbon monoxide *vs.* the C–O absorption frequencies[8] for these five metal carbonyls is shown in Fig. 1. This shows that the activation energy for the dissociation of carbon monoxide from a metal carbonyl increases with an increase in the metal–carbon bond order.

Experimental

Materials.—Small samples of $[Rh(P(C_6H_5)_3)_2COCl]$ and $[Rh(P(C_6H_5)_3)_2COCl_3]$ were generously supplied by Dr. Vallarino. Additional material as needed was prepared by the method of Vallarino[1] and of Chatt and Shaw.[9] The compounds were characterized by their analyses and infrared spectra. The quaternary ammonium salt, benzyldimethyl{2-[2-(*p*-1,1,3,3-tetramethylbutylphenoxy)ethoxy]ethyl}ammonium chloride (Hyamine 1622) was obtained from Rohm and Haas Chemical Co., Philadelphia, Pa. The radiocarbon monoxide was purchased from Tracerlab, Inc., Chicago, Ill.

Determination of Rates.—The apparatus used and the technique employed were the same as previously described.[10] Also, the same method was used for the treatment of the data observed. In order to make certain that the compound remained unchanged during exchange, the infrared spectra of the solutions were determined before and after exchange. In every case the initial spectrum did not change during the period of carbon monoxide exchange. The spectra were measured on a Baird-Associates Model AB-2 double beam recording spectrophotometer with NaCl optics.

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[4] F. Basolo, M. L. Morris, and R. G. Pearson, *Discussions Faraday Soc.*, **29**, 80 (1960).

[5] J. V. Rund, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, **3**, 658 (1964).

[6] R. J. Angelici and F. Basolo, *J. Am. Chem. Soc.*, **84**, 2495 (1962).

[7] G. Pajaro, F. Calderazzo, and R. Ercoli, *Gazz. chim. ital.*, **90**, 1486 (1960).

[8] The antisymmetric stretch for the four CO groups in the plane of $Mn(CO)_5X$ is chosen because it most closely corresponds to that for $Cr(CO)_6$; see L. Orgel, *Inorg. Chem.*, **1**, 25 (1962). It is also one of the four CO groups in the plane that is replaced during reaction; see ref. 6.

[9] J. Chatt and B. L. Shaw, *Chem. Ind.* (London), 290 (1961).

[10] F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961).

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Infrared Spectra and Structure of the Hexanitrocobalt Complex Salts

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The structures of hexanitrocobalt complex salts, $M_3[Co(NO_2)_6]$, have been studied by X-ray analysis.[1] It has been shown that the crystal structure of the K, Rb, and Cs salts is cubic and the molecular symmetry of one complex ion is T_h as shown in Fig. 1a. However, so far no structural analysis has been made for the Na salt.

We have measured the infrared spectra of hexanitrocobalt complex salts and found, as shown in Fig. 2, that the spectrum of the Na salt is different from those of the K, Rb, and Cs salts in the following points. (1) An appreciable difference is observed in the region 1450–1300 cm.$^{-1}$ where the NO_2 stretching vibrations appear. (2) The band near 830 cm.$^{-1}$ is assigned to the NO_2 scissoring vibration. Two sharp bands are observed for the vibration in the spectrum of the Na salt, whereas only one is found for the K, Rb, and Cs salts. (3) A striking difference is observed for the cobalt–nitrogen stretching vibration. The Na

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[1] M. Driel and H. J. Verweell, *Z. Krist.*, **A95**, 308 (1936).