TABLE IV

ENERGETIC DATA FOR TRANSITION METAL IONS PRODUCED FROM SOME METAL CARBONYLS

| | | Excited ion | | |
|---|---|---|---|---|
| Ion | $\Delta H_f$(ion),[12] kcal./mole | State | Excitation energy, kcal./mole | $\Delta H_f$-[$(M^+)^*$], kcal./mole |
| $Cr^+$ | 237 | $d^5\ ^2I_{11/2}$ | 86 | 323 |
| $Mo^+$ | 327 | $d^5\ ^2I_{11/2}$ | 66 | 393 |
| $W^+$ | 387 | $d^5\ ^2I_{11/2}$ | 69 | 456 |
| $Fe^+$ | 278 | $d^7\ ^2H_{11/2}$ | 58 | 336 |
| $Ni^+$ | 279 | | | |

nickel carbonyl case is less satisfactory and it appears reasonable to assume that only a portion of this is due to kinetic energy. (However, this may also reflect that an excited state is formed for the nickel case, but that the electronic configurations for the nickel in the ion and in the molecule ion are not the same.) A further study measuring the kinetic energy of the nickel ion produced from nickel carbonyl would be of significant interest.

## Conclusions

In the earlier study of nickel and iron carbonyls,[2] we proposed that the fragmentation of the transition metal carbonyls occurs by successive removal of CO groups. The observed features of the clastograms obtained in the present study of the group VIA carbonyls lend further support to this proposal and make even more desirable a test of this proposal by use of the quasi-equilibrium theory.[14,15]

Ions of the type $MC^+$ and $MC_2O^+$ are found to be produced by electron impact in the chromium, molybdenum, and tungsten carbonyls; similar ions were not observed in the spectra of nickel tetracarbonyl and iron pentacarbonyl. No ions of the type $MO^+$ were detected in the spectra of either the group VIA carbonyls or the nickel and iron carbonyls.

We have observed that the relative abundances of the $M(CO)_x^+$ species, where $x$ is 3, 4, or 5, increase as the atomic number of the metal atom increases. The same phenomenon is noted in the ions formed by cleavage of the C–O bond, *i.e.*, $MC^+$ and $MC_2O^+$.

The ionization potentials of the three hexacarbonyls are quite similar, but do show a slight increase with the atomic number of the central metal atom. This follows the trend in the variation of the ionization potential of the group VIA elements as the atomic number increases. Also, the ionization potentials of these carbonyls are not greatly different from the ionization potentials of the corresponding gaseous metals. It would appear, therefore, that the electron removed from the group VIA and VIII carbonyls upon ionization is one largely associated with the metal atom rather than with the carbonyl groups.

The large discrepancies between the experimentally determined heats of formation of the gaseous metal ions have been attributed to these ions being formed in excited states.

Several of these suggestions demand further investigation. It is anticipated that current studies in our laboratories on other carbonyls will aid in providing further insight into the bonding and stabilities of the transition metal carbonyls.

(14) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci.*, **38**, 667 (1952).

(15) M. Vestal, A. L. Wahrhaftig, and W. H. Johnston, *J. Chem. Phys.*, **37**, 1276 (1962).

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# Preparation and Properties of a Series of Halocarbonylrhodates

BY L. M. VALLARINO[1]

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Halocarbonyl anions of Rh(I) and Rh(III), of the formulas $[Rh(CO)_2X_2]^-$ (X = Cl, Br, I), $[Rh_2(CO)_2X_4]^{-2}$ (X = Br, I), and $\{Rh(CO)I_4\}^-$, are reported. These anions were isolated as the tetrabutylammonium and tetraphenylarsonium salts, and their structures were deduced from magnetic, conductivity, and infrared absorption measurements.

## Introduction

Halocarbonylmetalates are known[2-7] for several of the transition elements which form carbonyl halides. However, no halocarbonyl anions of rhodium have been reported, although its dimeric carbonyl halides, $[Rh_2(CO)_4X_2]$ (X = Cl, Br, I) have been known for more than 20 years[8] and extensively studied.[9] It was therefore of interest as part of an investigation on the coordination compounds of rhodium[10-14] to attempt the preparation of halocarbonylrhodates and to study

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[1] Chemistry Department, Florida State University, Tallahassee, Fla.

[2] R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 1860 (1956).

[3] L. Malatesta and M. Angoletta, *J. Inorg. Nucl. Chem.*, **8**, 273 (1958).

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[11] L. M. Vallarino, *ibid.*, 2287 (1957).

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[13] L. M. Vallarino, *J. Inorg. Nucl. Chem.*, **8**, 289 (1958).

[14] L. M. Vallarino, *Gazz. chim. ital.*, **89**, 1632 (1959).

TABLE I

FORMULAS, ANALYTICAL DATA, AND SOME PROPERTIES OF HALOCARBONYLRHODATES

| Compound | Color | M.p. (dec.), °C. | C, % |  | H, % |  | N, % |  | CO, % |  | Conductivity,[b] $\Lambda_M$, ohm.$^{-1}$ cm.$^2$ mole$^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |  |
| $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$ | Pale yellow needles | 81 | 45.7 | 46.0 | 7.7 | 7.5 | 3.0 | 3.2 | 11.8 | 11.6 | 29.5 |
| $[(C_4H_9)_4N][Rh(CO)_2Br_2]$ | Pale yellow needles | 86 | 38.5 | 38.75 | 6.9 | 6.6 | 2.5 | 2.7 | 10.0 | 10.1 | 29.1 |
| $[(C_4H_9)_4N][Rh(CO)_2I_2]$ | Mustard yellow leaflets | 78 | 32.95 | 33.2 | 5.5 | 5.8 | 2.15 | 2.4 | 8.5 | 8.2 | *c* |
| $[(C_4H_9)_4N]_2[Rh_2(CO)_2Br_4]$ | Orange-red needles | 174 | 38.1 | 38.1 | 6.8 | 6.5 | 2.6 | 2.8 | 5.2 | 4.8 | 33.8<br>($\Lambda_\infty$ = 44.4) |
| $[(C_4H_9)_4N]_2[Rh_2(CO)_2I_4]$ | Reddish brown leaflets |  | 32.45 | 32.3 | 5.8 | 5.9 | 2.2 | 2.15 | 4.45 | 4.0 | *c* |
| $[(C_4H_9)_4N]\{Rh(CO)I_4\}$[a] | Dark brown leaflets |  | 23.2 | 23.5 | 4.1 | 4.4 | 1.6 | 1.9 | 3.18 | 2.9 | *c* |
|  |  |  | Halogen, % |  | Rh, % |  |  |  |  |  |  |
|  |  |  | Calcd. | Found | Calcd. | Found |  |  |  |  |  |
| $[(C_6H_5)_4As][Rh(CO)_2Cl_2]$ | Pale yellow plates | 181 | 11.5 | 11.6 | 16.8 | 17.2 |  |  | 9.1 | 9.3 | 29.2 |
| $[(C_6H_5)_4As][Rh(CO)_2Br_2]$ | Yellow plates | 150 | 22.7 | 22.8 | 14.6 | 14.7 |  |  | 8.0 | 8.0 | 28.3 |
| $[(C_6H_5)_4As][Rh(CO)_2I_2]$ | Light brown leaflets | 121 | 31.9 | 31.8 | 12.9 | 12.5 |  |  | 7.0 | 6.75 | 25.5 |
| $[(C_6H_5)_4As]_2[Rh_2(CO)_2Br_4]$ | Deep red leaflets | 250–260 | 23.7 | 23.9 | 15.3 | 14.95 |  |  | 4.2 | 4.1 | 36.5 |
| $[(C_6H_5)_4As]_2[Rh_2(CO)_2I_4]$ | Reddish brown leaflets |  | 33.05 | 33.4 | 13.4 | 13.1 |  |  | 3.65 | 3.6 | *c* |
| $[(C_6H_5)_4As]\{Rh(CO)I_4\}$ | Dark brown leaflets |  | 53.61 | 54.1 | 10.87 | 10.4 |  |  | 2.96 | 2.5 | *c* |

[a] Calcd.: I, 57.6; Rh, 11.7. Found: I, 58.0, Rh, 11.5. [b] In $10^{-3}$ *M* nitrobenzene solution at 25°. [c] Solutions decompose on standing.

their properties. The preliminary results of this investigation have been reported,[15] and the present paper describes in detail a series of halocarbonyl anions of rhodium(I) and rhodium(III).

## Experimental

Table I lists the compounds prepared, together with their colors and crystal forms, melting or decomposition temperatures, analytical data, and molar conductivities. Table II reports schematically the preparations of the halocarbonylrhodates and their correlations.

**Tetrabutylammonium Dichlorodicarbonylrhodate(I) $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$.**—The starting material, $[Rh_2(CO)_4Cl_2]$, was prepared according to the method of Hieber, *et al.*,[8] and was recrystallized from boiling hexane. The orange-red needles thus obtained (0.6 g.) were dissolved in methanol (20 ml.) containing concentrated hydrochloric acid (3 ml.). The clear pale yellow solution which resulted was treated with a methanol solution of tetrabutylammonium chloride (1.0 g.) and concentrated to a small volume under reduced pressure. A precipitate formed, which was filtered off, washed with 10% aqueous hydrochloric acid, and then dried *in vacuo* over solid potassium hydroxide. Recrystallization from benzene by dilution with hexane yielded 1.0 g. of pale yellow $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$.

The compound is insoluble in water and hexane, moderately soluble in ethyl ether and benzene, and readily soluble in methylene chloride, chloroform, nitrobenzene, acetone, methanol, and ethanol. In the crystalline state the compound remains unaltered for several months; in alcohol and in acetone solution it is stable for several days in the presence of some hydrochloric acid, but in neutral solution it darkens slowly. The compound is immediately decomposed by strong alkali but not by concentrated hydrochloric acid even on boiling. It reacts with triphenylphosphine to form the complex $[Rh(CO)\{(C_6H_5)_3P\}_2Cl]$, and with 4-methoxyphenyl isocyanide and sodium perchlorate in ethanol to form the salt $[Rh(CH_3OC_6H_4NC)_4]ClO_4 \cdot C_2H_5OH$. The reaction with arylisocyanides, carried out by mixing the solid compound with liquid isocyanide, is accompanied by the rapid and complete evolution of carbon monoxide and was used for its quantitative determination.

**Tetrabutylammonium Dibromodicarbonylrhodate(I), $[(C_4H_9)_4N][Rh(CO)_2Br_2]$,** was prepared with 75% yield as described for its chloro analog, from $[Rh_2(CO)_4Br_2]$, hydrobromic acid, and $[(C_4H_9)_4N]Br$ in methanol at 0°. The chlorocarbonyl, $[Rh_2(CO)_4Cl_2]$, can also be used as the starting material, since the exchange of chlorine with bromine is rapid and complete. The salt $[(C_4H_9)_4N][Rh(CO)_2Br_2]$ was also prepared by dissolving $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$ in ice-cold methanol containing hydro-

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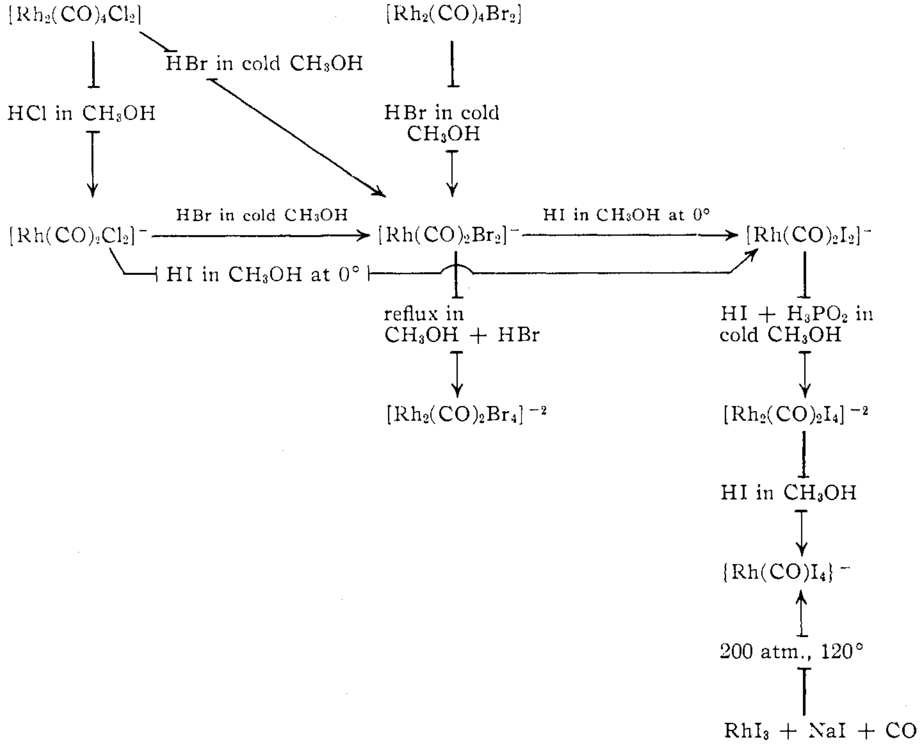
[15] L. M. Vallarino, "International Conference on Coordination Chemistry," Special Publication No. 13, The Chemical Society, London, 1959, p. 123.

TABLE II
CORRELATION TABLE OF HALOCARBONYLRHODATES



bromic acid and then concentrating the solution under reduced pressure until the product separated (yield 90%). Preparation and crystallization were carried out as rapidly as possible to avoid formation of some dinuclear $[(C_4H_9)_4N]_2[Rh_2(CO)_2Br_4]$.

**Tetrabutylammonium Diiododicarbonylrhodate(I), $[(C_4H_9)N][Rh(CO)_2I_2]$,** was prepared from $[Rh_2(CO)_4Cl_2]$, iodine-free hydriodic acid, and $[(C_4H_9)_4N]I$ in methanol at 0°, as described for the corresponding bromo compound, The pure product, obtained in 80% yield, was not recrystallized. The compound was also prepared by dissolution of $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$ or $[(C_4H_9)_4N][Rh(CO)_2Br_2]$ in ice-cold methanol containing iodine-free hydriodic acid, followed by rapid precipitation of the product with ice-cold water. In solution the compound loses carbon monoxide rapidly to give the dinuclear $[(C_4H_9)_4N]_2[Rh_2(CO)_2I_4]$ and, in the absence of a suitable reducing agent, oxidizes to $[(C_4H_9)_4N]\{Rh(CO)I_4\}$.

**Tetrabutylammonium Tetrabromodicarbonyldirhodate(I), $[(C_4H_9)_4N]_2[Rh_2(CO)_2Br_4]$.**—A saturated solution of $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$ in methanol containing 10% of concentrated aqueous hydrobromic acid was refluxed for 1 hr. On cooling crystals separated which were filtered off, washed with 2 ml. of ice-cold methanol, and dried *in vacuo* over solid potassium hydroxide. The pure product, obtained in 75% yield, could be recrystallized without decomposition from methanol containing hydrobromic acid. The compound has a solubility and a general chemical behavior similar to that of $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$. Unlike the latter, however, it does not quantitatively evolve carbon monoxide by reaction with 4-methoxyphenyl isocyanide, unless heated to 120°.

**Tetrabutylammonium Tetraiododicarbonyldirhodate(I), $[(C_4H_9)_4N]_2[Rh_2(CO)_2I_4]$.**—The salt $[(C_4H_9)_4N][Rh(CO)_2I_2]$ was dissolved in a minimum volume of methanol containing 5% of concentrated aqueous hydriodic acid (iodine-free) and 1% of hypophosphorous acid and allowed to stand at room temperature for 30 min. After concentration under reduced pressure, a precipitate formed which was filtered off, washed twice with 1 ml. of ice-cold methanol, and dried *in vacuo* over potassium hydroxide. The product (yield 25%) was shown to be pure by its infrared spectrum. Attempts to recrystallize it were unsuccessful as partial oxidation to $[(C_4H_9)_4N]\{Rh(CO)I_4\}$ occurred.

**Tetrabutylammonium Tetraiodocarbonylrhodate(III), $[(C_4H_9)_4N]\{Rh(CO)I_4\}$.**—The compound was obtained by the followin two methods.

**(A).**—A solution of $[(C_4H_9)_4N][Rh(CO)_2I_2]$ or $[(C_4H_9)_4N]_2[Rh_2(CO)_2I_4]$ in methanol containing hydriodic acid was refluxed for 10 min. (or allowed to stand at room temperature for several hours). After concentration under reduced pressure and dilution with ice-cold water, a precipitate formed which was filtered off, washed twice with several ml. of methanol, and dried *in vacuo* over potassium hydroxide. The product, recrystallized from methanol by dilution with water, was dried *in vacuo* over phosphoric anhydride (yield 65%). The solubility of this compound is similar to, but lower than, that of $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$.

**(B).**—Finely ground black $RhI_3$ (prepared from freshly precipitated rhodium(III) hydroxide and dilute hydriodic acid) was mixed with five times its weight of sodium iodide, placed in a glass vessel in an autoclave, and treated for 24 hr. with dry carbon monoxide at 200 atm. and 120°, in the presence of copper wire as halogen acceptor. A brown-black solid mass was obtained, and no deposit was observed on the clean surface of the copper wire or on the outer wall of the glass vessel, indicating no reduction of rhodium(III). The reaction mixture was extracted repeatedly with boiling methanol, and the filtered brown extract was treated with an excess of $[(C_4H_9)_4N]I$ and concentrated under reduced pressure. The dark brown precipitate which formed was filtered off, washed with water and ice-cold methanol, and then recrystallized as described above (yield 15%).

**Tetraphenylarsonium salts** were prepared similarly to the corresponding tetrabutylammonium salts, which they closely resemble except for a lower solubility in organic solvents.

**Conductivity measurements** were carried out by the usual procedure in nitrobenzene at 25°. The solutions of the iodo compounds became slightly cloudy on standing and their conductivity values varied with time.

**Magnetic susceptibility measurements** were carried out by the Gouy method on the powdered compounds at room temperature. All compounds are diamagnetic.

**Infrared spectra** (4000–250 cm.$^{-1}$ region) were recorded with a Perkin-Elmer Model 221 spectrophotometer, and the compounds

TABLE III

INFRARED ABSORPTION FREQUENCIES[a] (CM.$^{-1}$) OF THE HALOCARBONYLRHODATE ANIONS[b]

| Compound | CO str. sym. | CO str. antisym. | RhCO deform. out-of-plane | RhC str. sym. | RhCO bend. in-plane | RhC str. antisym. | RhCl str. |
|---|---|---|---|---|---|---|---|
| $[(C_4H_9)_4N][Rh(CO)_2Cl_2]$ | 2058 vs | 1974 vs | 619 s | 496 vs |  | 456 vw | 320 s, br; 290 s, br |
| $[(C_6H_5)_4As][Rh(CO)_2Cl_2]$ | 2060 vs | 1975 vs | 617 s | 495 vs |  | *c* | 318 s, br; 290 s, br |
| $[(C_4H_9)_4N][Rh(CO)_2Br_2]$ | 2062 vs | 1985 vs | 604 s | 492 s | 481 m | 446 w |  |
| $[(C_6H_5)_4As][Rh(CO)_2Br_2]$ | 2055 vs | 1975 vs | 604 s | 489 s | *c* | *c* |  |
| $[(C_4H_9)_4N][Rh(CO)_2I_2]$ | 2052 vs | 1985 vs | 585 s | 484 s | 465 m | 432 m |  |
| $[(C_6H_5)_4As][Rh(CO)_2I_2]$ | 2043 vs | 1967 vs | 582 s | 481 s | *c* | 433 m |  |
|  |  |  | Other bands |  |  |  |  |
| $[(C_4H_9)_4N]_2[Rh_2(CO)_2Br_4]$ | 2096 vs |  | 524 s |  |  |  |  |
| $[(C_6H_5)_4As]_2[Rh_2(CO)_2Br_4]$ | 2096 vs |  | 524 s |  |  |  |  |
| $[(C_4H_9)_4N]_2[Rh_2(CO)_2I_4]$ | 2058 vs |  |  |  |  |  |  |
| $[(C_6H_5)_4As]_2[Rh_2(CO)_2I_4]$ | 2058 vs |  |  |  |  |  |  |
| $[(C_4H_9)_4N]\{Rh(CO)I_4\}$ | 2070 vs |  |  |  |  |  |  |
| $[(C_6H_5)_4As]\{Rh(CO)I_4\}$ | 2070 vs |  |  |  |  |  |  |

[a] s, strong; m, medium; w, weak; v, very; br, broad. The reported values are those obtained in Nujol mulls and agree within experimental error with those in KBr disks. [b] The absorptions typical of the cations are listed in the Experimental section. [c] Region obscured by strong $[(C_6H_5)_4As]^+$ absorption.

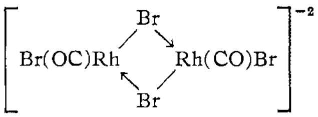
were examined both in Nujol mulls and in KBr disks. The anion absorptions and their assignments are listed in Table III. The absorption frequencies (cm.$^{-1}$) of the tetrabutylammonium and tetraphenylarsonium ions, obtained from their halide salts, follow. $[(C_4H_9)_4N]^+$: 2995 sh, 2964 vs, 2950 sh, 2920 sh, 2880 m, 1470 vs, 1460 sh, 1452 sh, 1383 m, 1370 sh, 1330 w, 1242 w, 1169 m, 1111 m, 1070 w, 1033 w, 995 m, 900 m, 884 m, 798 w, 738 m, 526 w, 397 vw. $[(C_6H_5)_4As]^+$: (the 3000 cm.$^{-1}$ region was not examined) 1575 w, 1476 m, 1438 s, 1316 w, 1186 w, 1160 vw, 1084 s, 1000 s, 780 w, 740 vs, 690 vs, 685 s, 474 sh, 463 s, 360 m, br (nonresolved), 350 m, br (nonresolved).

## Results and Discussion

Rhodium(I) halocarbonyls, $[Rh_2(CO)_4X_2]$ (X = Cl, Br), although nonpolar in character, readily dissolve in cold water containing halogen acids, without evolution of carbon monoxide. This behavior suggests the formation of a water-soluble halocarbonyl compound with acidic character, but attempts to isolate such a compound by evaporating the solution to dryness under reduced pressure at 0° were unsuccessful. However, upon addition of suitable organic cations, such as tetrabutylammonium, $[(C_4H_9)_4N]^+$, and tetraphenylarsonium, $[(C_6H_5)_4As]^+$, the salts of the anion $[Rh(CO)_2X_2]^-$ (X = Cl, Br, I) separated from the concentrated solution in good yields. These salts are crystalline diamagnetic substances, and in nitrobenzene solution show the electrical conductivity (Table I) typical of 1:1 electrolytes. Similar to the analogous Ir(I) anions, $[Ir(CO)_2X_2]^-$, and to the other tetracoordinated compounds of Rh(I) of $d^8$ electronic configuration, the anion $[Rh(CO)_2X_2]^-$ can be assigned a square-planar structure, and the presence of two strong absorptions in the CO stretching region of its infrared spectrum indicates a *cis* configuration.

The salts of the $[Rh(CO)_2Cl_2]^-$ anion are stable in the solid state and in solutions containing small amounts of hydrochloric acid, but in neutral solutions they discolor and decompose completely within a few hours. A similar behavior has been observed for the salts of the $[Pt(CO)Cl_3]^-$ anion.[2,16] The $[Rh(CO)_2Cl_2]^-$ anion is rapidly attacked by strong oxo acids and alkali and does not react at room temperature with ammonia and amines; with triarylphosphines and arylisocyanides it reacts immediately to give the complexes[10,11] $[Rh(CO)(R_3P)_2Cl]$ and $[Rh(RNC)_4]Cl$ (R = aryl), respectively. The chlorine atoms of $[Rh(CO)_2Cl_2]^-$ are readily replaced by bromine and iodine, in agreement with the known fact that the tendency of the halogens to coordinate to group VIII heavy elements in low oxidation states increases from chlorine to iodine.

The anions $[Rh(CO)_2Br_2]^-$ and $[Rh(CO)_2I_2]^-$ generally resemble in their behavior and properties the corresponding chloro analog. However, $[Rh(CO)_2Cl_2]^-$ is not affected by prolonged boiling in a solution made up of one volume of concentrated aqueous hydrochloric acid and one volume of methanol (50% HCl–methanol), $[Rh(CO)_2Br_2]^-$ decomposes on standing 1 day at room temperature or on refluxing for 1 hr. in 10% HBr–methanol, and $[Rh(CO)_2I_2]^-$ completely decomposes on standing 1 hr. at 0° in 10% HI–methanol. In acid solution containing $Br^-$ ions, the anion $[Rh(CO)_2Br_2]^-$ loses carbon monoxide to form the dinuclear $[Rh_2(CO)_2Br_4]^{-2}$, the salts of which are well-crystallized diamagnetic substances, stable in the solid state and in solutions containing small amounts of hydrobromic acid. The conductivity of these salts in nitrobenzene falls in the range of 1:2 electrolytes and their infrared spectra show a single strong absorption in the CO stretching region, thus suggesting the symmetrical formula



A similar formula can be assigned to the analogous iodo anion $[Rh_2(CO)_2I_4]^{-2}$, the salts of which are rather unstable in solution and did not give reliable conductivity data.

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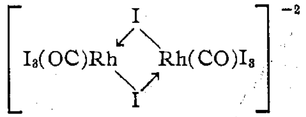
(16) R. J. Irving and E. A. Magnusson, *J. Chem. Soc.*, 2018 (1957).

The anion $[Rh_2(CO)_2I_4]^{-2}$ rapidly oxidizes in a solution containing $I^-$ ions, unless a suitable reducing agent is present, to form a Rh(III) iodocarbonyl anion of composition $\{Rh(CO)I_4\}^-$. The same anion is formed by the reaction of a mixture of $RhI_3$ and NaI with carbon monoxide at high temperature and pressure. The $\{Rh(CO)I_4\}^-$ anion, though comparatively more stable than the Rh(I) iodocarbonyl anions, decomposes slowly in solution and no reliable conductivity measurements could be obtained for its tetrabutylammonium and tetraphenylarsonium salts. In the absence of direct evidence, one might tentatively assign to the Rh(III) anion the symmetrical binuclear formula



which would agree with the usual coordination number of Rh(III) and with the presence of only one CO stretching band in the infrared spectrum of the anion. However, the corresponding Ir(III) anion, on the basis of its solution behavior, was assigned[7] the mononuclear formula $[Ir(CO)I_4]^-$.

The infrared absorption frequencies of the halocarbonylrhodate anions are listed in Table III. Assignments were made by comparison of the spectra with one another and with the spectra of other carbonyl compounds. The tetrabutylammonium salts, whose spectra are free from cation bands in the regions where the anion absorptions are expected to occur, were used as the basis for the investigation; the tetraphenylarsonium salts were used as a check.

The effect of the different halides on the strength of the carbon monoxide to rhodium bonds in the $[Rh(CO)_2X_2]^-$ anions should show indirectly in their infrared spectra. For square-planar halocarbonyl complexes such as $[Ir(CO)_2X_2]^-$, $[Pt(CO)_2X_2]$, $[Pt_2(CO)_2X_4]$, and $[Pt(CO)X_3]^-$, where X is Cl, Br, or I, it was found[4,5b,17] that the CO stretching frequency, and therefore the CO bond order, decreases in the order $Cl > Br > I$. For the $[Rh(CO)_2X_2]^-$ anions, however, the splitting between the symmetric and antisymmetric CO and RhC stretching vibrations, rather than their absolute frequency value, is expected to reflect the influence of the halide X. As the polarizability and the π-bonding ability increase from chlorine to iodine, the interaction between the symmetric and antisymmetric modes of $[Rh(CO)_2X_2]^-$ should decrease for the CO stretching and increase for the RhC stretching vibrations. The observed values are in fact: $\Delta\nu$ ($C{\equiv}O$) = 84, 77, and 69 cm.$^{-1}$ for the chloro, bromo, and iodo compounds, respectively, and $\Delta\nu$ (Rh—C) = 40, 47, and 52 cm.$^{-1}$ in the same order. On the other hand, the interaction among the bending RhCO modes should not be appreciably influenced by the halide and the observed values, in the above order, are: $\Delta\delta$ ($Rh{-}C{\equiv}O$) = 125, 123, and 120 cm.$^{-1}$. Finally, as the mass of the halide decreases, a less satisfactory agreement is observed between the number of bands present in the spectra of $[Rh(CO)_2X_2]^-$ and the number expected on the usual assumption that the vibrations of the OC–Rh–CO system are virtually independent from those of the X–Rh–X system. Since the masses of CO and Cl are comparable, the absorptions of the chloro compound would be more appropriately, though less simply, described as arising from vibrations of the ion as a whole.

Perhaps the most remarkable feature of the series of halocarbonylrhodates reported in this paper is that they so well conform to the expected behavior. Thus, the formation of the $[Rh(CO)_2X_2]^-$ anion results from the cleavage of the double halogen bridge of $[Rh_2(CO)_4X_2]$ by the incoming ligand $X^-$, similar to the well-known reactions of dimeric halogen-bridged complexes[17,18] of Pt(II) and Pd(II), the latter isoelectronic with Rh(I). For the square-planar ion $[Rh(CO)_2X_2]^-$, the *cis* configuration is expected to be the more stable[19] because of the π-bonding character of carbon monoxide. Also, the tendency of $[Rh(CO)_2X_2]^-$ to lose carbon monoxide and form the binuclear anion $[Rh_2(CO)_2X_4]^{-2}$ increases from chlorine to iodine, in the order of the *trans* effect and bridging ability of these halides. Finally, the spontaneous oxidation of the iodocarbonylrhodates(I) in the presence of iodide ions to give the Rh(III) derivative $\{Rh(CO)I_4\}^-$ is in agreement with both the lower oxidation–reduction potential and the lower electronegativity of iodine in comparison with chlorine and bromine.

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