of 7 was noticeable after 2-3 days and could be followed by infrared spectroscopy in the 3600-3400- and 1800-1500-cm^{-1} regions. For instance, the band at 1723 cm^{-1} (ν(C=O) of -COOH) decreased in intensity with time, while a band at 1651 cm^{-1}, formerly the weakest band for a freshly prepared sample in this spectral region, became much more intense. These changes could be explained by the change from "free" -COOH to -COOAg which accompanied the decomposition.

The new compounds described in this report all show at least limited solubility in water to form brown solutions, with complexes **1**, **4**, and **9** being the most soluble of the series. These solutions are remarkable in their stability toward water reduction to silver(I) species, especially the mixed dipic-terpy complexes. It has previously been noted that aqueous solutions of silver(II) compounds[18,24] show drastic decompositions of 25-50% or greater after only a couple of hours. Some measure of the enhanced stability of certain of the complexes described in the present report is the observation that an aqueous solution of Ag(dipicH)(terpy)-$(S_2O_8)_{1/2}\cdot 2H_2O$ (5.9×10^{-4} *M*) still retained some characteristic silver(II) color after 3 months. Apparently, the solubility and/or stability of the mixed-ligand complexes in water is enhanced by two factors: (1) their higher coordination number as contrasted with most silver(II) species and (2) the strong stabilizing influence of 2,2',2''-terpyridyl in these complexes.

Registry No. Ag(dipic)(terpy)$\cdot 4H_2O$, 12799-09-6; Ag(dipic)(bipy)$\cdot 3H_2O$, 12799-06-3; Ag(dipic)(phen)$\cdot {}^7/_2H_2O$, 12799-07-4; [Ag(dipicH)(terpy)]$[S_2O_8]_{0.5}$, 12799-10-9; [Ag(pic)(terpy)]$[S_2O_8]_{0.5}\cdot 2H_2O$, 37337-85-2; [Ag(quinH)(terpy)]$[S_2O_8]_{0.5}$, 12799-11-0; [Ag(lutH)(terpy)]$[S_2O_8]_{0.5}$, 12799-12-1; [Ag(isocinchH)(terpy)]$[S_2O_8]_{0.5}$, 12799-13-2; [Ag(dipcH)(terpy)]ClO_4, 37337-86-3; $[Ag(terpy)_2][S_2O_8]\cdot 3H_2O$, 37337-87-4; $Ag(lutH)_2\cdot 2H_2O$, 36926-56-4; Ag(dipic)$(dipicH_2)\cdot 4H_2O$, 36900-76-2; 2,2'-bipyridyl, 366-18-7; Ag(terpy)S_2O_8, 12565-92-3; $Ag(pic)_2$, 14783-00-7.

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Mercury-201 Nuclear Quadrupole Resonance. I. Mercury and Halogen Nqr in the Mercuric Halide Dioxanates

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^{201}Hg and halogen nqr have been observed in the 1:2 complexes of mercuric chloride and bromide with 1,4-dioxane. Since some confusion has arisen in the literature as a result of failure to distinguish between the 1:2 and 1:1 mercuric chloride-dioxane complexes, the reported halogen resonances of the 1:1 dioxane complexes of mercuric chloride, bromide, and iodide were verified. Additionally, the $\pm{}^3/_2 \longleftrightarrow \pm{}^5/_2$ transition for ^{127}I in the 1:1 mercuric iodide complex was observed and its frequency measured. No ^{201}Hg nqr was observed in any of the 1:1 complexes or in mercuric bromide itself although the apparently only other known ^{201}Hg nqr frequency, that of mercuric chloride, was confirmed. The changes in the halogen and mercury nqr frequencies upon complexation are interpreted, employing the usual Townes-Dailey approach, in terms of the effects of substituting oxygen for halogen in the highly distorted octahedral coordination about mercury which is found in all the compounds herein.

Introduction

In 1954, Dehmelt, Robinson, and Gordy reported the ^{201}Hg ($I = {}^3/_2$) nuclear quadrupole resonance (nqr) frequency for mercuric chloride, as well as the chlorine frequencies.[1] That report apparently remains the only observation of ^{201}Hg nqr until the present work. Other, unspecified, mercury compounds were examined by the previous workers but without success.

At the initiation of a program of ^{201}Hg nqr, we turned to the mercuric halide dioxanates since the available structural data, *i.e.*, the X-ray structure determination of the 1:1 complex of mercuric chloride with 1,4-dioxane[2] and that of the 1:2 complex of mercuric bromide with this ligand,[3] indicate that the mercuric chloride complexes should represent fairly weak perturbations of the one system in which ^{201}Hg nqr had been observed. Furthermore, the 1:2 complexes represent an instance in which linear HgX_2 units are isolated from one another in the solid state, unlike the halides themselves in which intermolecular mercury-halogen coordination occurs to varying degrees. Thus a more direct comparison of mercury-halogen covalent bonds, uncomplicated by mercury-halogen coordination, might be obtained from measurements on these complexes. Finally, halogen nqr had already been observed in many of these complexes.[4-6]

Of the six complexes in this set, the 1:1 and 1:2 complexes of mercuric chloride, bromide, and iodide with 1,4-dioxane, all are known compounds except for the 1:2 complex of mercuric iodide and we have been unable to obtain any evidence that it exists at room temperature. The mercuric iodide-dioxane system is thus straightforward but the existence of (at least) two distinct complexes for each of the other

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(1) H. G. Dehmelt, H. G. Robinson, and W. Gordy, *Phys. Rev.*, 93, 480 (1954).

(2) O. Hassel and J. Hvoslof, *Acta Chem. Scand.*, 8, 1953 (1954).

(3) M. Frey and J. Monier, *Acta Crystallogr., Sect. B*, 27, 2487 (1971).

(4) D. E. Scaife, *Aust. J. Chem.* 24, 1753 (1971).

(5) T. B. Brill, *J. Inorg. Nucl. Chem.*, 32, 1869 (1970).

(6) D. Biendenkapp and A. Weiss, *Z. Naturforsch. A*, 19, 1518 (1964).

two halides has led to some confusion in the past.

This is particularly so as interconversion of the 1:1 and 1:2 complexes of either halide is facile: gain or loss of 1 mol of dioxane occurs readily, depending on the presence or absence of excess dioxane. The 1:1 complexes will lose 1 further mol of dioxane in the air to give the uncomplexed halides but this is a much slower process. In keeping with the complete instability of its 1:2 complex, the 1:1 complex of mercuric iodide decomposes more rapidly than the other two 1:1 complexes.

A recent communication has clarified some of the problems in the thermochemistry of these complexes.[7] Barnes has shown that the chloride complex studied by Crenshaw[8] in 1938 was in fact the 1:2 complex and not the 1:1 complex. With the correct data for the 1:1 chloride complex the stability order of the 1:1 complexes is found to be chloride > bromide > iodide.[7] We find also (see Experimental Section) that, qualitatively, the 1:2 complex of mercuric chloride is slightly more stable with respect to the corresponding 1:1 complex than is the 1:2 bromide complex.

It thus seems reasonable that the complexes of a given stoichiometry are of similar structure and the discussion is based on this assumption though with the *caveat* that the X-ray data are incomplete. This assumption is likely to be most valid in the case of the 1:2 complexes, in which there is no mercury–halogen coordination. As will be seen in the Discussion, the differences in this factor account for much of the differences between one mercury–halogen system and another.

Experimental Section

The 1:2 complexes of mercuric chloride[9,10] and bromide[3] were obtained by recrystallizing the halides from dioxane, either by cooling a hot solution or by allowing a saturated solution to evaporate at room temperature. In the case of mercuric chloride, although some 1:1 complex may come out while the solution is still fairly hot, by the time it has cooled to room temperature, the 1:2 complex[9] is obtained. In the case of mercuric bromide, however, the 1:1 complex is initially obtained by cooling a hot solution but upon standing in dioxane at room temperature rapid (*ca.* 1 hr) conversion to the 1:2 complex occurs. Therefore slow evaporation of a solution at room temperature[3] gives the 1:2 complex for both halides. Mercuric iodide gives the 1:1 complex[5,8] by either technique. These results were obtained with the aid of halogen nqr. The 1:1 complexes of mercuric chloride[5,7,9,10] and bromide[5,8] were obtained either by decomposing the 1:2 complexes or, more conveniently, from the halide and excess dioxane in acetone.

All the complexes were analyzed by measuring the weight loss due to removal of dioxane (1 *and* 2 moles for the 1:2 complexes). Satisfactory analyses were obtained in all cases. The 1:2 complexes were conveniently analyzed by means of a Du Pont 950 thermogravimetric analyzer operated isothermally at ambient temperature in tandem with a Du Pont 900 differential thermal analyzer. The sample could be placed in the apparatus while still moist with dioxane and a break in the slope of the weight–time curve observed when simple evaporative loss of uncomplexed dioxane was complete. Another such break occurred when conversion to the 1:1 complex was complete. This could in turn be decomposed by a brief heating to the pure halide.

Rough estimates of the relative stabilities of the complexes may be made from the rates at which dioxane is lost under similar circumstances. In the open air at room temperature, conversion of small samples (*ca.* 0.5 g) of the 1:2 complex to the 1:1 complex takes about 1 hr, with the bromide being somewhat more rapid than the chloride. Conversion of the 1:1 iodide complex to mercuric iodide under these conditions takes less than 6 hr. The other two 1:1 complexes require substantially longer, approximately 1 week for the bromide complex and 10 days for the chloride complex, to convert completely to the pure halides. This ratio of times was preserved at 90° where the 1:1 chloride complex required 90 min for complete loss of dioxane and the 1:1 bromide complex only 1 hr.

Table I.[a,b] Nqr Data

Compd	Nqr freq, MHz	
	^{201}Hg	Halogen (^{35}Cl, ^{79}Br, ^{127}I)
$HgCl_2$	354.08 ± 0.05[c]	22.2303 ± 0.0008[d,e]
	354.21 ± 0.06[d]	22.0505 ± 0.0005
$HgCl_2$(diox)		20.454 ± 0.005[f,g]
$HgCl_2$(diox)$_2$	323.38 ± 0.05[c]	21.15 ± 0.02[g,h]
		21.21 ± 0.02[g,i]
$HgCl_2$(dione)		21.51 ± 0.02[c]
$HgBr_2$		153.74 ± 0.02[e,j]
		157.86 ± 0.02
$HgBr_2$(diox)		160.03 ± 0.02[f,g]
$HgBr_2$(diox)$_2$	313.23 ± 0.05[c]	170.07 ± 0.02[c]
HgI_2 (yellow)		159.95 ± 0.02[e,f]
		161.82 ± 0.02
HgI_2(diox)[m]		172.77 ± 0.02[f,g,k]
		333.53 ± 0.05[c,l]

[a] diox = 1,4-dioxane; dione = cyclohexane-1,4-dione. [b] Data at room temperature unless otherwise indicated. [c] This work. [d] Reference 1. [e] Crystallographic doublet. [f] Reference 5. [g] Confirmed in this work. [h] Reference 4 (assumed therein to be the 1:1 complex). [i] At 77°K; ref 6 gives 21.196 MHz (assumed therein to be the 1:1 complex). [j] D. Nakamura, Y. Vehara, Y. Kurita, and M. Kubo, *J. Chem. Phys.*, **31**, 1433 (1959). [k] $\pm{}^1/_2 \longleftrightarrow \pm{}^3/_2$ transition. [l] $\pm{}^3/_2 \longleftrightarrow \pm{}^5/_2$ transition. [m] $e^2Qq/h = 1117.9$ MHz; $\eta = 0.168$.

The ^{201}Hg nqr data were taken using a superregenerative spectrometer employing a coaxial cavity. Nqr signals could be detected with both magnetic and frequency modulation. The former was used almost exclusively as it gave a good signal to noise ratio and a very flat base line. The oscillator could be either self-quenched or externally quenched and both methods gave comparable signals. The halogen data, except for the $\pm{}^5/_2 \longleftrightarrow \pm{}^3/_2$ transition of iodine which was taken with the coaxial spectrometer, were collected using the automatic spectrometers described by Peterson and Bridenbaugh.[11]

Results

All the nqr data for these compounds, both mercury and halogen, now available are collected in Table I. The values for the mercuric chloride-dioxane complexes previously reported from three different laboratories are discordant since both Scaife[4] and Weiss[6] were in fact working with the 1:2 complex although they assumed that they had the 1:1 complex. (The situation is further complicated by the fact that the net temperature coefficient of the 1:2 complex between 77°K and room temperature is nearly zero.) In view of these possibilities, we have checked all the halogen nqr data for the complexes. The values of Brill[5] for the 1:1 complexes are in all cases correct. Additionally, we have measured the previously unreported bromine nqr frequency for the 1:2 bromide complex and the $\pm{}^3/_2 \longleftrightarrow \pm{}^5/_2$ transition for ^{127}I in the 1:1 iodide complex. This allows a determination of the asymmetry parameter (η) and a precise determination of the nuclear quadruple coupling constant (e^2Qq/h) for the ^{127}I nucleus.[12]

We were able to confirm the literature value for the ^{201}Hg nqr frequency of mercuric chloride[1] and to obtain this number for the 1:2 complexes of mercuric chloride and bromide with dioxane. The nqr spectrum of the chloride complex is displayed in Figure 1. It was observed that the halogen resonances of the 1:2 complexes are singularly sharp and strong, much more so than those of the 1:1 com-

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(7) J. C. Barnes, *Inorg. Chem.*, 11, 2267 (1972).

(8) J. L. Crenshaw, A. C. Cope, N. Finkelstein, and R. Rogan, *J. Amer. Chem. Soc.*, 60, 2308 (1938).

(9) S. G. K. Nair and S. S. Moosath, *Proc. Indian Acad. Sci., Sect. A*, 47, 344 (1958).

(10) P. A. Laurent and E. Arsenio, *Bull. Soc. Chim. Fr.*, 618 (1958).

(11) G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Instrum.*, 35, 698 (1964); 36, 702 (1965).

(12) R. Livingston and H. Zeldes, "Table of Eigenvalues for Pure Quadrupole Spectra, Spin 5/2," Report No. 1913, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1955.

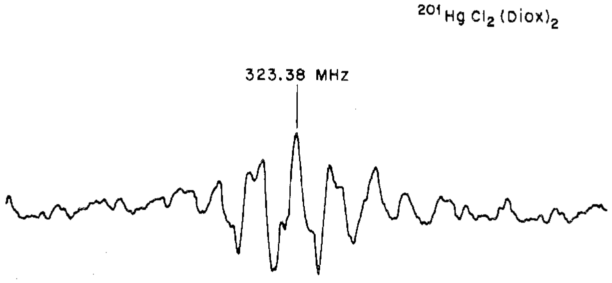

Figure 1. ^{201}Hg nqr in the 1:2 complex of mercuric chloride with 1,4-dioxane. Data were taken using a coaxial-cavity, self-quenched superregenerative spectrometer. Magnetic field modulation was employed and the RC time was 3 sec.

plexes and somewhat more than those of the uncomplexed halides. If the mercury resonances in the other compounds are similarly broadened, they might easily have proved undetectable.

Discussion

The halides themselves (mercuric chloride,[13] mercuric bromide,[14] and the yellow, high-temperature form of mercuric iodide[15]) exhibit in the solid state a highly distorted octahedral coordination about mercury in which the linear HgX_2 units are essentially equatorially surrounded by four more halogens at much greater distances. Each halogen is thus coordinated to two mercury atoms in addition to the one to which it is principally bound. In the 1:1 complex of mercuric chloride with dioxane, two of these four secondary positions about mercury are occupied by dioxane oxygens (trans, from two different dioxane molecules) while the remaining two positions are still occupied by chlorines, each of which is now coordinated to only one mercury atom.[2] In the 1:2 complex of mercuric bromide with dioxane, all four secondary positions are occupied by dioxane oxygens, from four different dioxane molecules, and there is thus no mercury-halogen coordination.[3] The basic, linear HgX_2 units are preserved throughout from the uncomplexed halides to the 1:2 complexes.

The trends in the mercury and halogen nqr frequencies will be discussed in terms of the finer details of these structural changes and within the context of the following assumptions.

(1) The observed frequency changes directly reflect changes in the respective nuclear quadrupole coupling constants. That is, changes in the asymmetry parameters are assumed to be unimportant.

(2) The changes in the coupling constants or, equivalently, in the absolute values of the electric field gradients, are in turn attributed solely to changes in the absolute value of the valence shell "p-electron imbalance" of either mercury or halogen. This is the usual Townes-Dailey assumption[16] in its simplest form, the p-electron imbalance being defined simply as

$$N_z - {}^1/_2(N_x + N_y) \tag{1}$$

where the N_i are the populations of the respective p-orbitals, p_z being taken as the orbital lying along the major axis of the linear HgX_2 unit in all cases.

(3) The hybridization of mercury is taken as sp and that of halogen as pure p, with only σ bonds being considered.

All in all, three types of bonds in this series of compounds are of interest here: the principal mercury-halogen bonds (I), the secondary mercury-halogen coordinate bonds (II), and the mercury-oxygen coordinate bonds (III). An examination of expression 1 leads to some straightforward expectations. For a purely ionic, uncoordinated mercuric halide, $X^-Hg^{2+}X^-$, the coupling constants for both mercury and halogen should be zero since for mercury, $N_z = N_x = N_y = 0$ and for halogen $N_z = N_x = N_y = 2$ so that $N_z = {}^1/_2(N_x + N_y)$ and expression 1 is again zero. Thus weakening a type I bond should lower the observed nqr frequency for both nuclei.

On the other hand, weakening of the coordinate bonds should raise the nqr frequency for both types of nuclei since, in the absence of coordination, N_x and N_y occupy the extreme values of 0 and 2 for mercury and halogen, respectively, and as $0 \leqslant N_z \leqslant 2$ for both elements, the absolute value of expression 1 can only be reduced by deviation of N_x and N_y from their extreme values. (We assume that the coordinate bonds are weak relative to the primary bonds.) The same of course holds true for mercury in the mercury-oxygen coordinate bonds.

In proceeding from the uncomplexed halide to the 1:2 complex, all the bonds of type II are replaced by bonds of type III. Simply breaking all the type II bonds should increase the field gradient at both mercury and halogen but, since in the halide each mercury atom is coordinated to four halogens and each halogen to only two mercury atoms, the effect should be twice as great for mercury. Donation of electron density from oxygen into the p_x and p_y orbitals of mercury would mitigate this (electron density equal to half that originally provided by the coordinate bonds to halogen would exactly compensate and the net increase would be the same for both mercury and halogen).

Changes in the type I bonds brought about by complexation should, on the other hand, affect both mercury and halogen to the same degree since here the fact that each mercury atom is bonded to two halogens in this manner is exactly compensated for by the fact that the mercury sp orbitals are only half p. The type I bonds should be strengthened by simple breakage of the type II bonds but of course formation of the type III bonds will have the opposite effect. Clearly, the key factor is the relative strengths of the type II and type III bonds.

In going from mercuric chloride to its 1:2 complex with dioxane, the data in Table I show that the chlorine nqr frequency decreases, from the average of the crystal field doublet of mercuric chloride to the single value of the complex, by 4.5%. The corresponding decrease in the mercury resonance is nearly twice this, 8.6%. Thus if no significance is attributed to the type II bonds in mercuric chloride, a 4.5% drop in the mercury resonance is due to weakening of the type I bonds upon complexation and a further 4.1% is due to the direct effects of electron donation from oxygen.

That the type II bonds in the chloride series are, however, not completely insignificant is indicated by the value of the chlorine resonance in the 1:1 complex, in which only half of the type II bonds of mercuric chloride have been replaced by type III bonds. This resonance is 7.6% below the average for mercuric chloride or 3.1% of this value below that of the 1:2 complex. Most of this 3.1% rise on going from the 1:1 complex to the 1:2 complex seems attributable to the breaking of the remaining coordinate bond of each chlorine.

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(13) D. Grdenic, *Ark. Kemi*, **22**, 14 (1950).

(14) (a) H. J. Verweel and J. M. Bijvoet, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **77**, 122 (1931); (b) H. Braekken, *ibid.*, **81**, 152 (1932).

(15) G. A. Jeffrey and M. Viasse, *Inorg. Chem.*, **6**, 393 (1967).

(16) (a) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York, N. Y., 1969, Chapter 7; (b) T. P. Das and E. L. Hahn, *Solid State Phys., Suppl.*, No. 1 (1958).

The type II bonds in the 1:1 complexes are, moreover, likely to be stronger than those in the halides since each halogen is participating in only one coordinate bond in the complex. This seems to be borne out by the X-ray structure of the complex in which the coordinate mercury-chlorine bond is shorter than the similar (but unequal) bonds in mercuric chloride.

It also seems reasonable that the type III bonds in the 1:1 complex are stronger than those in the 1:2 complex (the mercury-oxygen distance is shorter in the 1:1 chloride complex than in the 1:2 bromide complex) and even that the total electron donation from oxygen is not much greater in the 1:2 complex than in the 1:1 complex since the second molecule of dioxane is held so loosely, although all the type III bonds are equivalent in the 1:2 complex. The X-ray structure determination of the 1:1 complex of mercuric chloride with cyclohexane-1,4-dione[17] shows that there are no type II bonds in this complex, and its chlorine nqr frequency (Table I) is near that of the 1:2 dioxane complex, for which this is also true.

Mercuric bromide and its dioxane complexes represent a case in which the significance of the type II bonds is greater than in the chloride series. A clear measure of this is provided by the change in the halogen frequency upon going from the 1:1 complex to the 1:2 complex. Again, using the average value of the halogen doublet of the uncomplexed halide as a standard, an increase of 6.5% is observed in contrast to the 3.1% increase in the chloride system. Moreover, the greater strength of the type II bonds in the bromide series is such that an increase in the halogen nqr frequency is always observed upon replacing them with type III bonds. Thus the 1:1 complex is 3.7% higher in frequency than the halide and the 1:2 complex is fully 10.2% higher.

The smaller initial increase seems attributable to two factors: (1) strengthening of the type II bonds in the 1:1 complex over those in the halide and (2) a greater offsetting by electron donation from oxygen of the tendency of type I bonds to be strengthened by the rupture of type II bonds in the first complexation. A net strengthening of the type I bonds in the 1:2 bromide complex over those of mercuric bromide is evidenced by the relative bond lengths, shorter in the former. This strengthening of the type I bonds should partially compensate for the fact that stronger type II bonds must be broken upon complexation in the bromide series than in the chloride series.

The behavior of mercuric iodide is similar to that of mercuric bromide with an increase in the halogen frequency upon formation of the 1:1 dioxane complex. The increase, with respect to yellow mercuric iodide, is even greater, 7.4%, consistent with the still stronger type II bonds in the iodide series. The iodine asymmetry parameter in the complex is large enough (0.17) to suggest significant type II bonds. Also, the lower stability of the 1:1 iodide complex relative to those of the other two halides and the apparently complete instability of the 1:2 iodide complex are likely a result of the stronger type II bonds involved.

In sum, the correlation between the changes in the field gradients at the mercury and halogen nuclei and what is to be straightforwardly expected upon replacing half or all of the four secondary halogen coordination positions about mercury in the solid halides by dioxane oxygens seems at least qualitatively good. The substitution of oxygen for halogen affects the populations of the p_x and p_y orbitals of mercury and halogen directly and thus their p_z orbital populations indirectly. The observed nqr frequencies are determined by the net effect of these factors.

A final point concerns the comparison of mercury-chlorine and mercury-bromine bonds in the 1:2 complexes, in which mercury-halogen coordination is absent. The most straightforward comparison is obtained if it is assumed that the contribution from oxygen is the same in both complexes. While this question cannot definitely be settled at this point, the nqr and thermodynamic data indicate that the differences in the mercury-oxygen bonds are small. The differences between one halide series and another can be largely accounted for by differences in the importance of mercury-halogen coordination.

If this is the case, the mercury nqr frequency should be proportional to the p_z orbital population, *i.e.*, proportional to the halogen q/q_0, a number given by (if $\eta = 0$)

$$\frac{q}{q_0} = \frac{2 \times \text{obsd freq}}{\text{constant}} \tag{2}$$

where the constant is 109.8 MHz for chlorine and 769.8 MHz for bromine.[16] The ^{201}Hg frequency of the 1:2 bromide complex should then be simply

$$\frac{170.07}{769.8} \times \frac{109.8}{21.15} \times 323.28 = 370.8 \text{ MHz} \tag{3}$$

or 15% higher than that of the 1:2 chloride complex. However, it is observed to be only 3% lower.

This situation is not unique. The ^{197}Au nqr frequencies for gold(I) chloride[18] and iodide[19] are nearly the same. In dialkylaluminum halides it has been found that the nature of the halogen has little effect on the ^{27}Al quadrupole coupling constant.[20] Further examples are yielded by Mossbauer quadrupole splittings. Those of ^{197}Au in triphenylphosphinegold(I) chloride and bromide are similar[21] (that of the iodide is slightly greater) and in an extensive analysis of tin quadrupole splitting, it was concluded that the effects of chlorine and bromine are not significantly different (although that of iodine is).[22]

It seems then that metal-halogen bonds, particularly those of chlorine and bromine, are more similar than either the relative metal-halogen electronegativity differences or, where available, the halogen q/q_0 values indicate. In the case of the latter a possible explanation lies in the constants used in expression 2, which are simply the quadrupole coupling due to a single electron (actually a single hole) in a valence shell p orbital in the atomic halogen. Their use in expression 2 implies that a p orbital in the atomic state is equivalent to one in a molecular solid, which is unlikely to be strictly true. Moreover, the difference between an atomic p orbital and a molecular one could easily differ from one element to the next.

The result of this is that although q/q_0 may constitute an adequate measure of the relative degree of covalency in a series of compounds of a given halogen, it is less reliable as an absolute measure of covalence in comparing one halogen with another. Here the constant factor, the other element, is likely to be more reliable.

As for the factor of electronegativity difference, it seems

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[17] P. Groth and O. Hassel, *Acta Chem. Scand.*, 18, 1327 (1964).

[18] P. Machmer, M. Read, and P. Cornil, *Inorg. Nucl. Chem. Lett.*, 3, 215 (1967).

[19] P. Machmer, *J. Inorg. Nucl. Chem.*, 30, 2627 (1968).

[20] M. J. S. Dewar, D. B. Patterson, and W. I. Simpson, *J. Amer. Chem. Soc.*, 93, 1030 (1971).

[21] J. S. Charlton and D. I. Nichols, *J. Chem. Soc. A*, 1484 (1970).

[22] M. G. Clark, A. G. Maddock, and R. H. Platt, *J. Chem. Soc., Dalton Trans.*, 281 (1972).

empirically that other parameters, such as σ^* which is nearly the same for bromine and chlorine,[23] may be more reliable guides to polar effects in quadrupole coupling. Good correlations of σ^* with tin Mossbauer splittings have been claimed.[24]

(23) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, Chapter 13.

Registry No. $HgCl_2$(diox), 27104-48-9; $HgCl_2(diox)_2$, 39152-02-8; $HgCl_2$(dione), 39152-03-9; $HgBr_2$(diox), 28630-99-1; $HgBr_2(diox)_2$, 39152-05-1; HgI_2(diox), 28631-00-7.

(24) (a) R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, **4**, 65 (1970); (b) R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, 2145 (1969).

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Kinetic Studies of Thermal Decomposition and Substitution Reactions of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) Compounds. A Competitive Study of Lewis Bases for the Intermediate $[Mo(CO)_4P(C_6H_5)_3]$

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Kinetic and mechanistic studies of thermal decomposition and substitution reactions of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) (where amine = NHC_5H_{10} or NC_5H_5) are reported. Substitution reactions have been carried out for a variety of entering ligands (L) to form *cis*-$Mo(CO)_4[P(C_6H_5)_3]L$ compounds. These substitution reactions proceed *via* the rate expression: rate = $k[Mo(CO)_4[P(C_6H_5)_3](amine)]$, at low concentrations of L. When L is a strongly nucleophilic ligand and is employed at high concentrations, a second-order term must be added to give a rate expression of the form: rate = $[k + k'[L]][Mo(CO)_4[P(C_6H_5)_3](amine)]$. Competitive reactions for the intermediate $[Mo(CO)_4P(C_6H_5)_3]$ have been investigated for a number of ligands (L) including carbon monoxide, phosphines, and amines. There are only slight differences in the rate constants for the reactions of the $[Mo(CO)_4P(C_6H_5)_3]$ intermediate with various ligands L. Substitution equilibria are however dependent on the nature of L. Steric factors have been shown to be important in these substitution reactions; *e.g.*, for the sterically bulky ligand L = (*o*-tolyl)$_3$P no substitution product is observed.

Introduction

Previously we have reported upon the kinetics of thermal decomposition and substitution reactions of $M(CO)_5$(amine) compounds of group VIb metals.[2] In order to study the role of electronic and steric factors in these types of reactions we have examined the kinetics and mechanism of thermal decomposition reactions of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) (where amine = NHC_5H_{10} or NC_5H_5) to form $Mo(CO)_5P(C_6H_5)_3$ and *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$. This reaction proceeds by a rate-determining step involving dissociation of the amine ligand which is first order in starting complex and produces $Mo(CO)_5P(C_6H_5)_3$, *cis*-$Mo(CO)_4[P(C_6H_5)_3]_2$, and insoluble solids as products.

In the presence of Lewis bases L, such as amines, phosphines, phosphites, arsines, and carbon monoxide, the intermediate $[Mo(CO)_4P(C_6H_5)_3]$ species is trapped in the form of *cis*-$Mo(CO)_4[P(C_6H_5)_3]L$ complexes. This substitution can also proceed by an SN2 mechanism (step 3 in eq 1).

Competitive studies employing a variety of group Va ligands, as well as carbon monoxide, were investigated in order to determine the reactivity of the $[Mo(CO)_4P(C_6H_5)_3]$ species toward the different Lewis bases.

The experimental results indicate that the steric properties of the incoming L group are very important. For example,

$$\begin{tikzcd}
\mathit{cis}\text{-}Mo(CO)_4[P(C_6H_5)_3](NHC_5H_{10}) \arrow[r, shift left, "k_1"] \arrow[dd, "k_3"', "L"] & {} \arrow[l, shift left, "k_{-1}"] \\
 & {[Mo(CO)_4P(C_6H_5)_3] + NHC_5H_{10}} \arrow[dl, "L"', "\text{fast}\ k_2"] \\
\mathit{cis}\text{-}Mo(CO)_4[P(C_6H_5)_3]L &
\end{tikzcd} \quad (1)$$

no substitution was observed when L = $P(o\text{-}CH_3C_6H_4)_3$, even with a very large excess of the organophosphorus ligand present. In addition the intermediate $[Mo(CO)_4P(C_6H_5)_3]$ appears to have a slightly greater affinity toward a softer nucleophilic reagent.

Experimental Section

Materials. Molybdenum hexacarbonyl was the generous gift of Climax Molybdenum Co. and was used without further purification. The tertiary phosphite 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]-octane was donated by Arapahoe Chemicals, Boulder, Colo., and was sublimed before use. ^{13}CO was purchased from Monsanto Research Corp., Miamisburg, Ohio. Tetrahydrofuran (THF) was distilled over lithium aluminum hydride just before use. Diglyme (bis(2-methoxyethyl) ether) was refluxed over sodium and then distilled. Piperidine was purified by vacuum distillation. Triphenylarsine and triphenylstibene were recrystallized from chloroform–methanol.

Preparation of *cis*-$Mo(CO)_4[P(C_6H_5)_3]$(amine) (amine = NHC_5H_{10} or NC_5H_5). The disubstituted molybdenum tetracarbonyl species were prepared photochemically in THF from $Mo(CO)_5P(C_6H_5)_3$ and the corresponding amines by the procedure previously described.[3] The products were purified by recrystallization from chloroform–methanol.

Spectral and Kinetic Measurements. All spectral measurements were recorded in *n*-hexane solvent. Infrared spectra (2100–1830 cm^{-1}) were obtained employing a Perkin-Elmer 521 grating spectro-

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(2) (a) D. J. Darensbourg, M. Y. Darensbourg, and R. J. Dennenberg, *J. Amer. Chem. Soc.*, **93**, 2807 (1971); (b) R. J. Dennenberg and D. J. Darensbourg, *Inorg. Chem.*, **11**, 72 (1972).