Correspondence

The Relative Stabilities of Noble Gas Compounds[1]

Sir:

Xenon appears to form bonds only with the most electronegative elements, fluorine and oxygen. It is reasonable to assume, therefore, that whatever type of binding exists in the xenon compounds it involves considerable electron transfer from the noble gas to the combining element. It follows that the tendency to form chemical bonds must increase with the atomic number of the rare gas.[2] This rationalization is supported by many facts, *viz.*, radon compounds do exist, krypton compounds are less stable than the corresponding xenon ones, etc.[3] Since compounds of the lighter noble gases have thus far not been obtained a further conclusion has gained almost general concensus: because of their high ionization potentials argon and the light noble gases are completely inert. This generalization is also substantiated by the MO calculations of Lohr and Lipscomb[4] and of Waters and Gray,[5] although the latter authors considered ArF_4 a possibility.

The author wishes to point out in this communication that the weight of the *chemical evidence* suggests that some argon compounds may be *more stable* than the corresponding compounds of krypton and, therefore, that there is a fair prospect of coaxing argon into forming relatively stable compounds.

It is well known that compounds of As, Se, and Br with the more electronegative elements (notably fluorine and oxygen) are *less stable* than the corresponding compounds of both their higher (Sb, Te, I) and lower homologs (P, S, Cl). Examples of this behavior are[6–8]: (i) The heats of atomization (in kcal. mole^{-1}) of the following gaseous oxides: SO_2 (240); SeO_2 (200); TeO_2 (216). (ii) The standard heats of formation (in kcal. mole^{-1}) of the following halides: SF_6(g) (−264); SeF_6(g) (−246); TeF_6(g) (−318); PF_3(g) (−189); AsF_3(g) (−189.4); SbF_3(g) (−216); PCl_3(g) (−71); $AsCl_3$(g) (−70.1); $SbCl_3$(g) (−91.2). (iii) The standard heats of formation (in kcal. mole^{-1}) of $HClO_3$, $HBrO_3$, and HIO_3 are −24, −12.5, and −56, respectively. (iv) SO_3 and TeO_3 are stable substances but SeO_3 is very unstable. Also, PCl_5 and $SbCl_5$ are known, but $AsCl_5$ was never obtained; SeF_4 is much less stable than either SF_4 or TeF_4. (v) The oxides of bromine are, in general, much less stable than the oxides of chlorine and iodine. (vi) Perchlorates (ClO_4^-) and periodates (IO_4^- and IO_6^{-5}) exist and are quite stable whereas perbromates were not obtained so far. To these facts, however, one must add that: (vii) This trend seems not to be obeyed by the interhalogen compounds.[9] Thus, although the dissociation energies of IF(g), BrF(g), and ClF(g) are, respectively, 66.2, 59.4, and 60.3 kcal. mole^{-1}, the standard heat of formation of BrF_3(g) is higher than that of ClF_3(g) (−67.1 and −38.8 kcal. mole^{-1}, respectively).

Sanderson[10] and Lakatos[11] have tried to rationalize these trends in terms of alternant electronegativities. Many years ago[12] the author tried to explain the nonexistence of the ion BrO_4^- in the following naïve way: in the periodates the low electronegativity of iodine stabilizes the contributing ionic structures and in the perchlorates the π-bond structures are stable due to the low double-bond repulsive forces[13] between chlorine and oxygen. The intermediate position of bromine with respect to both these two factors makes the BrO_4^- ion particularly unstable. Unless a low ionization potential is a particularly important factor in the noble gas compounds,[14] it is probable that the same unfavorable situation would be present in krypton–oxygen bonds as compared with xenon–oxygen and argon–oxygen bonds.

If this general chemical behavior is not reversed for the group 0 elements, it is to be expected that some compounds of argon may be about as stable as the corresponding krypton compounds. This is particularly true with the higher oxidation numbers and specially with oxygen compounds. These requirements may dim somewhat the prospects of obtaining chemically bonded argon species since the stability of the known noble gas compounds decreases with the oxidation number (Kr(VI) species are unknown) and also because until now xenates and perxenates have been obtained only through the xenon fluorides. However, recent measurements of the oxidation potentials of aqueous xenon[15] indicate that powerful oxidation agents should be able to oxidize xenon directly to oxygenated compounds, once

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[1] Work supported by grants from the U.S.A.F. Office of Scientific Research and the National Science Foundation.

[2] H. H. Hyman, *J. Chem. Educ.*, **41**, 174 (1964).

[3] H. H. Hyman, Ed., "Noble Gas Compounds," University of Chicago Press, Chicago, Ill., 1963.

[4] L. L. Lohr, Jr., and W. N. Lipscomb, *ibid.*, p. 347.

[5] J. H. Waters and H. B. Gray, *J. Am. Chem. Soc.*, **85**, 825 (1963).

[6] M. Schmeisser and K. Brandle, *Advan. Inorg. Chem. Radiochem.*, **5**, 41 (1963).

[7] J. W. George, *Progr. Inorg. Chem.*, **2**, 33 (1960).

[8] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, Oxford, 2nd Ed., 1950, p. 266.

[9] E. H. Wiebenga, E. E. Havinga, and K. H. Boswijk, *Advan. Inorg. Chem. Radiochem.*, **3**, 133 (1961).

[10] R. T. Sanderson, *J. Am. Chem. Soc.*, **74**, 4792 (1952); "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960.

[11] B. Lakatos, *Naturwissenschaften*, **41**, 355 (1954); *Z. physik. Chem.*, **206**, 41 (1956).

[12] R. Ferreira, *Bull. soc. chim. France*, 131 (1950).

[13] K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 2140 (1948).

[14] The importance of the low ionization potential of the central atom has been emphasized by Pitzer [*Science*, **139**, 414 (1963)] and quite recently by Coulson [*J. Chem. Soc.*, 1442 (1964)], but it is difficult to estimate where the critical value lies.

[15] E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964). The author wishes to thank Dr. Malm for sending him a preprint of his recent work.

the great activation energy barriers are overcome. The possibility that an argon–oxygen compound could also be formed without recourse to the fluorides cannot be ruled out, and from the foregoing one can conclude that species like $HArO_4^-$ and ArO_4 have a fair chance of being about as stable as, respectively, the known $HXeO_4^-$ ion and xenon tetroxide (XeO_4).[16]

(16) H. Selig, H. H. Claassen, C. L. Chernick, J. G. Malm, and J. L. Huston, *Science*, **143**, 1322 (1964).

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Chromium(VI) Species and Spectra in Acidic Solutions

Sir:

The first dissociation equilibrium quotient of H_2CrO_4, K_{11}, was first determined[1] from the apparent ab-

$$K_{11} = (HCrO_4^-)(H^+)/(H_2CrO_4) \qquad (1)$$

sorptivities[2] ($\bar{\epsilon}_1$) of monomeric Cr(VI), determined at different hydrogen ion concentrations, (H^+), in the investigation of dimerization of Cr(VI) in acidic solutions.

$$\bar{\epsilon}_1 = \frac{\epsilon_{11}(HCrO_4^-) + \epsilon_{12}(H_2CrO_4)}{(HCrO_4^-) + (H_2CrO_4)} = [\epsilon_{11}K_{11} + \epsilon_{12}(H^+)]/[K_{11} + (H^+)] \qquad (2)$$

where ϵ_{11} and ϵ_{12} are the molar absorptivities of $HCrO_4^-$ and H_2CrO_4, respectively. Since the ratios $\bar{\epsilon}_1/\epsilon_{11}$ at 25.0° in 1 *M* $HClO_4$, the most acidic solutions used, were only 0.922, 0.915, 0.909, and 0.911 at wave lengths 370, 380, 390, and 400 mμ, respectively, K_{11} was not determined with great precision. It was found that with the K_{11} value of 1.21 moles l.$^{-1}$ determined in this manner, it was necessary to postulate the existence of $HCr_2O_7^-$ in order to account for the dependence of the gross dimerization quotient, K', on (H^+), where

$$K' = (\text{total dimers})/(\text{total monomers})^2 \qquad (3)$$

The apparent absorptivities of dimeric Cr(VI), $\bar{\epsilon}_2$, which were determined with less accuracy than $\bar{\epsilon}_1$, did not show sufficient change with (H^+) to offer spectral evidence at these wave lengths for the existence of $HCr_2O_7^-$.

There is an alternate interpretation of the earlier data. If one assumes that in solutions of (H^+) 1 *M* or less, the only dimer present was $Cr_2O_7^{2-}$, one can calculate K_{11} from K', (H^+), and K_d since

$$K_{11} = (H^+)/[(K_d/K')^{1/2} - 1] \qquad (4)$$

where

$$K_d = (Cr_2O_7^{2-})/(HCrO_4^-)^2 \qquad (5)$$

The K_{11} values at 25.0° in solutions of unit ionic strength calculated using K_d = 98 are given in Table I.

TABLE I

K_{11} CALCULATED FROM K' WITH EQ. 4 AND K_d = 98

(H^+), *M*	Av. K'	K_{11}
0.277	86	4.10
0.416	81	4.16
0.693	72	4.16
1.000	64	4.21

The average K_{11} is 4.16 (standard deviation σ = 0.05). Since at the same (H^+), the ratio $(K_d/K')^{1/2}$ differs from unity more than the ratios $\bar{\epsilon}_1/\epsilon_{11}$ do, the calculation of K_{11} from K' is probably much more reliable than that from $\bar{\epsilon}_1$ if the assumption made concerning the dimeric Cr(VI) species is valid. Until other experimental evidence shows otherwise, this interpretation is as good as, if not better than, our previous one. The values of ϵ_{12} calculated from $\bar{\epsilon}_1$ using the new value of K_{11} are 589 (σ = 76), 405 (σ = 43), 250 (σ = 22), and 155 (σ = 18) M^{-1} cm.$^{-1}$ at 370, 380, 390, and 400 mμ, respectively.

Recently Haight, *et al.*,[3] reported a value for K_{11} of 6.5 at 25° and unit ionic strength calculated from $\bar{\epsilon}$ at wave lengths of 260 and 350 mμ. They used a Cr(VI) concentration of 4×10^{-4} g.-atom/l. and assumed that the concentrations of dimeric Cr(VI) were negligible. Their value of K_{11} at unit ionic strength is probably too large since they used in their calculation ϵ_{12} values, calculated from data at ionic strength 3.0, which were smaller than corresponding ϵ_{12} values calculated at ionic strength 1.0.

We have examined the absorption spectra of Cr(VI) at wave lengths 220–365 mμ carefully at much lower Cr(VI) concentrations. The removal of reducing impurities from water used, the preparation of solutions, and the spectrophotometric equipment were similar to those reported earlier,[1] except that the cell thermostating device has been improved. Reagent grade potassium dichromate was recrystallized.

A pair of solutions of unit ionic strength and 4.98×10^{-5} g.-atom/l. in Cr(VI) and 1.002 *M* and 0.001073 *M* in $HClO_4$, respectively (the ionic strength of the latter was maintained with $NaClO_4$), was carefully scanned at wave lengths 320–365 mμ at 5-mμ intervals at 25.0°. The ratio of the net absorbance of the more acidic solution to that of the less acidic solution, or approximately $\bar{\epsilon}_1/\epsilon_{11}$, decreased from 0.99 at 320 mμ to 0.93 at 365 mμ (0.94 at 350 mμ) and all were greater than those reported at wave lengths of 370–400 mμ. A second pair of solutions, similar to the first but containing only 2.00×10^{-5} g.-atom/l. of Cr(VI), was scanned at wave lengths of 220–292 mμ at 2-mμ intervals at 15.0°. The ratio ranged from 0.98 to 0.92 (0.93 at 260 mμ). Therefore, none of the wave lengths in the 220–365 mμ region examined offered a better $\bar{\epsilon}_1/\epsilon_{11}$ ratio for the determina-

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(1) J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **75**, 6180 (1953).

(2) The symbols of ref. 1 are used in the present report. All concentrations of Cr(VI) species were expressed in g.-atoms/l. and the absorptivities, ϵ, were calculated on that scale. Absorptivities were called extinction coefficients in ref. 1.

(3) G. P. Haight, Jr., D. C. Richardson, and N. Hall, paper presented before the 145th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1963; *Inorg. Chem.*, **3**, 1777 (1964).