
COMMUNICATIONS TO THE EDITOR

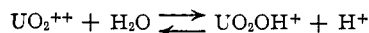
NEGATIVE WIEN EFFECTS

Sir:

We wish to report that solutions of uranyl nitrate and perchlorate of the order of 2×10^{-4} molar concentration exhibit a decrease in conductance upon the application of high electrical fields. This is in contrast with the usual behavior of electrolytes, for Max Wien¹ and all subsequent experimenters invariably have observed an increase of conductance of electrolytes under such circumstances. The decrease in conductance, expressed as the high field conductance quotient, $\Delta\lambda/\lambda(0)$, at 65° amounts to 1.3% at a field of 200 kilovolts/cm., and is many times greater than any possible experimental errors. The figure 1.3% is corrected for the Wien effect of the reference electrolyte, and should be considered a fractional change of conductance on the part of the uranyl nitrate or perchlorate alone. The phenomenon has not been observed with any other electrolytes thus far tested, including uranyl sulfate and fluoride.

The phenomenon is dependent upon temperature. Both uranyl nitrate and perchlorate exhibit small positive Wien effects at 5°, small negative Wien effects at 25° with multiple crossover of the zero conductance quotient axis as a function of increasing field, and at 65° a sizable negative Wien effect or decrease of conductance at all fields. It is also dependent upon pH. The uranyl salt solutions are themselves hydrolyzed, but if acid or base is purposely added, or if a strong electrolyte such as potassium nitrate is added, the magnitude and trend of the effect as a function of field is decidedly altered. The effect of adding acid is the most significant, decreasing the magnitude of the negative Wien effect.

The decrease in conductance with application of field may be due either to a decrease in the number of conducting ions or to an actual change in the method of conduction. These results and others to be reported later dealing with a high field conductance study of uranyl ion solutions² lead us to conclude that the reaction



the occurrence of which is favored by higher temperatures as part of the hydrolysis scheme of uranyl ion,³ is responsible for the phenomenon in these solutions. Under the influence of the applied field, hydrogen ion, with its abnormally high mobility, may be expected to overtake and collide with the slower-moving uranyl ions, reversing the above hydrolysis reaction and decreasing the number of conducting species. If such a mechanism is responsible, then it should be possible to demonstrate the phenomenon of negative Wien effects in other electrolytes, particularly with aquo complexes of transition metal ions. If a change in mechanism of conduction is involved,

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- (3) J. A. Hearne and A. G. White, *J. Chem. Soc.*, 3168 (1957).

it is not easy to predict in what kinds of chemical systems the decrease of conductance upon application of a field should be sought.

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STRUCTURE OF AND METAL-METAL BONDING IN $\text{Rh}(\text{CO})_2\text{Cl}$

Sir:

A detailed X-ray investigation of $\text{Rh}(\text{CO})_2\text{Cl}$ has produced results of unusual interest, which not only clarify previous work but also appear to provide some insight into the nature of bonding of the metal carbonyls and related compounds.

The compound, generously made available to us by H. Sternberg and I. Wender of the Bureau of Mines, was first prepared by Hieber and Lagally.¹ Their freezing point depression data established a dimeric species, $\text{Rh}_2(\text{CO})_4\text{Cl}_2$, in solution. Hieber and Heusinger² proposed a dimeric planar chlorine-bridge structure which has been accepted by others.^{3,4} From infrared studies both in solution and Nujol mull, Yang and Garland⁵ and later Hinds⁶ suggested a second possible model with only Rh-Rh bonds linking the dimers. Further infrared, magnetic susceptibility, and dipole moment studies by Wilt⁷ showed the compound to be diamagnetic with dipole moment $\mu = 1.64 \pm 0.03 D$ in benzene. Wilt⁷ postulated a third structure involving the intersection of two planar $\text{Rh}(\text{CO})_2\text{Cl}$ groups along the Cl-Cl line with a dihedral angle not equal to 180°.

Precession and Weissenberg pictures revealed the crystals to be tetragonal with lattice constants $a = 14.23 \text{ \AA}$, $c = 9.32 \text{ \AA}$. The calculated density for 16 $\text{Rh}(\text{CO})_2\text{Cl}$ species per unit cell is 2.74 g./cc. in good agreement with an experimental density of 2.72 g./cc. determined by the flotation method. The probable space group, $I\bar{4}2d$, was determined from systematic absences and the structure ultimately found. This space group has 16-fold general positions which results in one $\text{Rh}(\text{CO})_2\text{Cl}$ species in the asymmetric unit.

A complete three-dimensional Patterson analysis of intensity data taken with $\text{MoK}\alpha$ radiation located the rhodium positions; the other atoms were found from subsequent three-dimensional Fourier maps. Isotropic thermal refinement by

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- (2) W. Hieber and H. Heusinger, *Angew. Chem.*, **68**, 678 (1956).
- (3) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).
- (4) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1960, p. 309.
- (5) A. C. Yang and C. W. Garland, *J. Phys. Chem.*, **61**, 1510 (1957).
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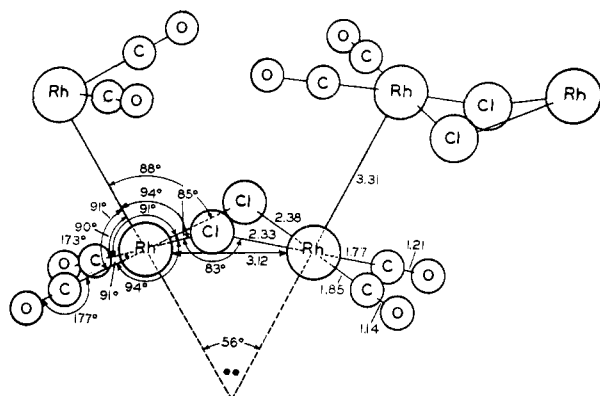


Fig. 1.—Bond lengths and angles in $\text{Rh}(\text{CO})_2\text{Cl}$.

least squares⁸ resulted in a final discrepancy factor of $R_1 = 6.7\%$ for 239 observed reflections.

The principal features of the structure are given in Fig. 1. Two essentially planar $\text{Rh}(\text{CO})_2\text{Cl}$ groups intersect at an angle of 124° . The resulting dimers apparently are linked by direct Rh-Rh bonds to form infinite chains. A Rh-Rh distance of 3.31 Å. is consistent with X-ray data for other metal-metal bonds⁹⁻¹¹ which involve the coupling of unpaired electrons. In order to explain the compound's diamagnetism in the solid state we propose a second so-called bent metal-metal bond as indicated in Fig. 1 which would result from the overlap of d^2sp^3 hybridized σ -type orbitals at an angle of approximately 56° . Evidently in solution the weak metal-metal bonds break to give dimeric molecules. The interatomic distances and angles are in accord with the proposed octahedral environment about each Rh atom. Semi-quantitative molecular orbital arguments¹² for bent metal-metal bonding involving primarily p orbitals have been presented for $\text{Co}_2(\text{CO})_6\text{-C}_2(\text{C}_6\text{H}_5)_2$.^{13,14}

Our work on $\text{Rh}(\text{CO})_2\text{Cl}$ suggests that bent metal-metal bonding involving octahedral hybridization occurs in $\text{Co}_2(\text{CO})_8$ ¹⁵ and $\text{Co}_2(\text{CO})_9\text{C}_2\text{H}_2$.¹⁶ In fact octahedral coordination rather than square pyramidal coordination¹⁷ readily can be rationalized from the structural results for $\text{Fe}_2(\text{CO})_2(\text{CO})_6\text{-C}_2\text{Me}_2$ ^{18,19} and $\text{Fe}_3(\text{CO})_8[(\text{C}_6\text{H}_5)_2\text{C}_2]_2$.²⁰

On the basis of infrared and dipole moment measurements Hieber and Beck²¹ proposed that di-

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meric compounds of the type $[\text{Fe}(\text{CO})_2\text{X}]_2$ ($\text{X} = \text{S}, \text{Se}, \text{SC}_2\text{H}_5, \text{SeC}_2\text{H}_5$) possess chalcogen bridges and non-planar configurations. Our results support this proposal, and we furthermore believe that these compounds possess bent metal-metal bonds.

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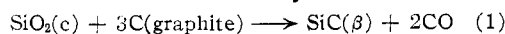
RECEIVED FEBRUARY 20, 1961

THE FREE ENERGY OF SILICA

Sir:

Experimental data on certain metallurgical reactions at high temperatures point to an error in the presently accepted value for the free energy of SiO_2 . Four distinct groups of data lead to the same conclusion.

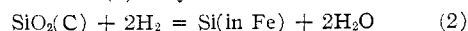
I.—Kay and Taylor¹ have repeated the earlier measurements of Baird and Taylor² on the reaction



According to their measurements the equilibrium pressure of CO reaches 1 atm. at 1800°K . Using the accepted values³ for the free energy of SiO_2 and CO, the equilibrium data lead to a free energy of SiC which is less negative by 5 kcal. than that found by Humphrey, Todd, Coughlin and King.⁴ The data of the latter investigators have received experimental confirmation in the work of Chipman, Fulton, Gokcen and Caskey⁵ and more recently that of Kirkwood and Chipman⁶ using measurements of the solubility of SiC in molten iron and lead, respectively. The agreement suggests that the equilibrium of reaction (1) be used to calculate the free energy of SiO_2 rather than the reverse calculation which has been reported by Smiltens.⁷

Using the tabulated data of Humphrey, *et al.*,⁴ for the free energy of β -SiC and the accurately known data for CO, the free energy of formation of SiO_2 at 1800°K . is -138.4 kcal. Coughlin³ gives -133.35 for cristobalite and essentially the same figure for the other crystalline forms. The equilibrium data thus lead to a result which is 5 kcal. more negative than the "third-law" value.

II.—When a molten Fe-Si alloy is equilibrated with an atmosphere of H_2 and H_2O in a silica crucible, equilibrium (2) may be established



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