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 COMMUNICATIONS TO THE EDITOR
 

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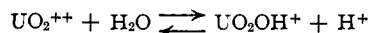
## NEGATIVE WIEN EFFECTS

Sir:

We wish to report that solutions of uranyl nitrate and perchlorate of the order of  $2 \times 10^{-4}$  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 Wien<sup>1</sup> 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 solutions<sup>2</sup> 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,<sup>3</sup> 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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- (2) J. F. Spinnler, Dissertation, Yale University, 1961.
- (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  
Rh(CO)<sub>2</sub>Cl
 

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Sir:

A detailed X-ray investigation of Rh(CO)<sub>2</sub>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.<sup>1</sup> Their freezing point depression data established a dimeric species, Rh<sub>2</sub>(CO)<sub>4</sub>Cl<sub>2</sub>, in solution. Hieber and Heusinger<sup>2</sup> proposed a dimeric planar chlorine-bridge structure which has been accepted by others.<sup>3,4</sup> From infrared studies both in solution and Nujol mull, Yang and Garland<sup>5</sup> and later Hinds<sup>6</sup> suggested a second possible model with only Rh-Rh bonds linking the dimers. Further infrared, magnetic susceptibility, and dipole moment studies by Wilt<sup>7</sup> showed the compound to be diamagnetic with dipole moment  $\mu = 1.64 \pm 0.03 D$  in benzene. Wilt<sup>7</sup> postulated a third structure involving the intersection of two planar Rh(CO)<sub>2</sub>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 Rh(CO)<sub>2</sub>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 Rh(CO)<sub>2</sub>Cl species in the asymmetric unit.

A complete three-dimensional Patterson analysis of intensity data taken with 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).
- (6) L. de C. Hinds, S.B. Thesis, M.I.T., May, 1958.
- (7) J. R. Wilt, S. B. Thesis, M.I.T., May, 1960.