least for halogenation reactions, the rates are comparable to collision rates, and random substitution seems to result. Hence a knowledge of the isomer possibilities seems even more important than would be the case if clear-cut directive influences were acting.

In Tables III and IV are shown all the possible isomers for $B_{10}H_{10-n}X_n{}^{2-}$ and $B_{12}H_{12-n}X_n{}^{2-}$. The numbering system is that employed by Muetterties, et al.[7] Table IV gives, in effect, all of the possible permutations of two kinds of objects at the vertices of an icosahedron. All of the possible geometries of carborane derivatives are thus also included, although because of the nonequivalence of all vertices in those structures, each $B_{12}H_{12-n}X_n{}^{2-}$ isomer corresponds to several isomers of $B_{10}C_2H_{12-n}X_n$.

No explicit consideration has been given to isomerism among products containing more than one kind of substituent. The number of isomers is, of course, enormous. The number of isomers of $B_{12}H_{10-m}$-$X_mY_2{}^{2-}$ is implicit in the total of the isomers for the three carboranes, using boron substitution only. Thus there are 11 isomers for $m = 1$, 57 for $m = 2$, 132 for $m = 3$, 246 for $m = 4$, and 278 for $m = 5$.

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Observations on the Complex between Uranyl and Chlorite Ions

BY GILBERT GORDON AND DAVID M. H. KERN

Chlorite is known to be a good oxidizing agent in aqueous solution,[1] but very little is known about its ability to form complexes with metal ions. During the course of some experiments in which aqueous solutions of uranium(IV) were being oxidized by $ClO_2{}^-$, a transient yellow color was observed. This color has been interpreted in terms of a complex between $UO_2{}^{2+}$ and $ClO_2{}^-$. The purpose of this report is to indicate the progress which has been made in studying the properties of this complex.

Experimental

In all of the measurements the quantity of interest was ΔA, the enhancement of absorbancy per cm. of cell length in the mixed acidic solutions of $UO_2{}^{2+}$ and $ClO_2{}^-$ compared to that on the basis of no interaction. Both $UO_2{}^{2+}$ and ClO_2, the decomposition product of $ClO_2{}^-$ in acid solution, are yellow and absorb light in the same spectral region as the observed uranium chlorite complex. Therefore, in this region, where all three species are absorbing, a blank solution containing each of these separately was run in the reference compartment *vs.* a cell containing the $UO_2{}^{2+}$-$ClO_2{}^-$ mixture. The hydrogen ion concentration and the ionic strength ($I = 1.00\ M$) were carefully matched in an attempt to minimize variation in activities. To effect changes in [H^+] and [$UO_2{}^{2+}$], sodium perchlorate was substituted for these species. The reference cell with $ClO_2{}^-$ contained Mg^{2+} in place of $UO_2{}^{2+}$ to maintain similar ionic media in the two cells.

Although $HClO_2$ disproportionates fairly rapidly to form ClO_2, this reaction is much slower than the formation of the $ClO_2{}^-$ complex. The rate law for the disproportionation reaction[2]

$$4HClO_2 = Cl^- + 2ClO_2 + ClO_3{}^- + 2H^+ + H_2O$$
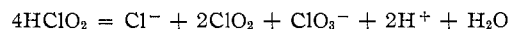
reported by Barnett is[2,3]

$$-d(HClO_2)/dt = k(HClO_2)^2$$

and the value of k at 25° is 1.4 l. mole^{-1} min.$^{-1}$.

To minimize the effect of ClO_2, the $ClO_2{}^-$ solutions of the appropriate ionic strength were injected simultaneously into the acidic solution of $UO_2{}^{2+}$ in the sample compartment and the solution of identical ionic strength and acidity containing Mg^{2+} substituted for $UO_2{}^{2+}$ in the reference compartment. This rapid injection and mixing was achieved by the use of matched spring-loaded syringes. The tandem firing of these syringes was within 10 msec. and the mixing time is less than 30 msec.[4] In this way the kinetic reaction of $ClO_2{}^-$ to form ClO_2, a species absorbing in the region of interest, was automatically subtracted from the observed spectra. By use of a reference cell containing $UO_2{}^{2+}$, simultaneous corrections were made for the uncomplexed $UO_2{}^{2+}$. The effect of Cl^- and $ClO_3{}^-$ on the $UO_2{}^{2+}$ spectrum was shown to be negligible. It was also shown that the slit width required to make this type of measurement was not large enough to introduce any errors.

Differences in zero time mixing were carefully checked by comparing blank solutions of perchloric acid into which $ClO_2{}^-$ was injected in both sample and reference compartments. Perfect mixing and timing should result in no change of absorbance as a function of time in the region of absorption of ClO_2. The blank experiments showed that the solutions could be matched to within 1% by this method. The spectra of the chlorite complex showed only very small changes with time, presumably due to errors in volume and zero time mixing, and none of the characteristics of the $UO_2{}^{2+}$ or ClO_2 spectra was evident. Changes as small as 5% in the $ClO_2{}^-$ concentration would have been detected as differences in rate of ClO_2 formation. Since differences of this type were not observed, it has been concluded that less than 5% of the $ClO_2{}^-$ has been used in complex ion formation.

The analytical procedures used to determine the concentration of $UO_2{}^{2+}$, $ClO_2{}^-$, and $HClO_4$ are the same as those described previously.[1a] All measurements were made at 25° using a Cary Model 14M spectrophotometer with a thermostated cell compartment using 2-cm. quartz cells.

Results and Discussion

Due to the absorption of light by $UO_2{}^{2+}$ and ClO_2 in the region of interest, the most meaningful data have been collected at 370 mμ, where these interferences could be minimized. These data are summarized in Table I.

The concentration of [$UO_2{}^{2+}$] and $\Sigma\ ClO_2{}^-$ given in Table I are the stoichiometric quantities of these species. The actual concentration of free $ClO_2{}^-$ and H^+ have been calculated from the equilibrium

$$HClO_2 = H^+ + ClO_2{}^-$$
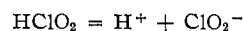
(1) (a) D. M. H. Kern and G. Gordon, "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, Ed., Pergamon Press, 1964, p. 655; (b) B. J. Fontana and W. M. Latimer, *J. Am. Chem. Soc.*, **69**, 2598 (1947).

(2) H. Taube and H. Dodgen, *ibid.*, **71**, 330 (1949).
(3) B. Barnett, Thesis, University of California, 1935.
(4) R. Thompson and G. Gordon, *J. Sci. Instr.*, submitted for publication.

TABLE I

$UO_2^{2+} \cdot ClO_2^-$ COMPLEX FORMATION IN PERCHLORIC ACID

2-cm. cell at 25°, $I = 1.00\ M$

$[UO_2^{2+}]$, M	$\Sigma\ ClO_2^-$, M	$[ClO_2^-]$, M	$[H^+]$, M	A_{obsd}	$Q\mathcal{E}_{370m\mu}$
0.20	0.0011$_0$	1.0 × 10^{-4}	0.10	0.214	0.535 × 10^4
0.179	0.00444$_4$	2.12 × 10^{-4}	0.200	0.379	0.499 × 10^4
0.00895	0.0138$_6$	2.97 × 10^{-3}	0.0367	0.264	0.497 × 10^4
0.0447$_8$	0.0138$_6$	4.14 × 10^{-4}	0.325$_3$	0.187	0.504 × 10^4
0.1343	0.0138$_6$	1.53 × 10^{-3}	0.0806	1.980	0.482 × 10^4
0.0447$_8$	0.0138$_6$	2.03 × 10^{-3}	0.0582	0.969	0.533 × 10^4
0.0600	0.0056$_0$	2.67 × 10^{-4}	0.200	0.165	0.515 × 10^4
0.0447$_8$	0.0138$_6$	3.77 × 10^{-3}	0.0268	1.592	0.472 × 10^4

using the dissociation constant $K_a = 1.1 \times 10^{-2}$.[2] The molar absorbancy, $\mathcal{E}$, is defined as $A = \mathcal{E}lC$ where A is the measured absorbance, C the molar concentration, and l the path length.

If the association between ClO_2^- and UO_2^{2+} is governed by the equilibrium

$$UO_2(H_2O)_n{}^{2+} + ClO_2^- = UO_2(H_2O)_{n-1}ClO_2{}^+ + H_2O$$
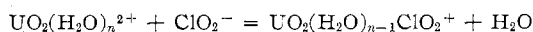
with an equilibrium constant Q where

$$Q = \frac{[UO_2 \cdot ClO_2{}^+]}{[UO_2^{2+}][ClO_2^-]}$$

the values of $Q\mathcal{E}_\lambda$ can be evaluated at various wave lengths using the expression

$$Q\mathcal{E}_\lambda = \frac{A_{obsd}/2}{[UO_2^{2+}][ClO_2^-]}$$

These values have been tabulated for a variety of initial reactant concentrations. Only some of the data have been included to indicate the concentration variables and the corresponding values of $Q\mathcal{E}_\lambda$; however, Table I does contain all the data points for the limiting concentrations. The average value of $Q\mathcal{E}_{370\ m\mu}$ from a series of 35 individual experiments was $0.49_7 \times 10^4$ $\pm\ 0.02_4 \times 10^4$. Additional values of $Q\mathcal{E}_\lambda$ as a function of wave length were as follows: 300 mμ, 0.41 × 10^4; 340 mμ, 0.901 × 10^4; 390 mμ, 0.40 × 10^4; 410 mμ, 0.21 × 10^4; and 430 mμ, 0.11 × 10^4.

The direct proportionality between the absorbancy enhancement and the product of the UO_2^{2+} and the actual ClO_2^- concentration persists over a wide concentration range. This demonstrates that a relatively small amount of the ClO_2^- and UO_2^{2+} is tied up in the complex under these conditions. Thus, it is not possible to evaluate both the molar absorbancy, $\mathcal{E}$, of the complex ion and the equilibrium quotient for the reaction in which it is formed, but only the product of the two. Absorption bands of complex ions in the ultraviolet region are usually due to allowed electronic transitions and the maximum extinction coefficients[5] appear to be on the order of 10^4–10^5. If this is used as an upper limit, using the data at 370 mμ, a lower limit can be assigned to Q of ≥0.02. This is reasonably consistent with a calculation based on the observation that less than 5% of the ClO_2^- was used in complex ion formation, suggesting that the $UO_2ClO_2^+$ complex is not a very stable species.

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A Crystalline Complex of Benzene and Tetrabutylammonium Perchlorate

BY R. P. SEWARD

In a measurement of the distribution of tetrabutylammonium perchlorate between benzene and water in which excess solid salt was present, the concentration of perchlorate in the benzene phase was found to be 0.00077 mole/kg. of solution at 25°. However, Luder, Kraus, Kraus, and Fuoss[1] had measured the electrical conductance of dry benzene solutions of tetrabutylammonium perchlorate at concentrations up to 0.013 M. This discrepancy in solubility, apparently due to water, occasioned the present investigation. The observations described below indicate that the discrepancy in solubility was not related to the presence of water but to the formation of a crystalline benzene–tetrabutylammonium perchlorate complex in the system where the low solubility was found.

Experimental

When tetrabutylammonium perchlorate (m.p. 210°) was added to dry benzene, two liquid layers were observed. Weighed samples, separated at 25°, were evaporated to dryness at 110°. The salt content of the upper layer was found to be 0.65 wt. % or 0.0168 M, while the lower layer was 38% salt. During the transfer of a two liquid phase system, which had been standing for several days, a rapid crystallization occurred and only a single liquid phase remained. The salt content of this liquid phase was but 0.00038 mole/kg. of solvent at 25°. When the crystalline material in contact with the liquid phase was warmed to 50° the crystals melted and the two liquid phases returned. When the system was cooled the crystalline material reappeared.

To establish the benzene content of the crystalline material, samples which had stood in a desiccator beside a 10 mole % solu-

(5) L. E. Orgel, "An Introduction to Transition-Metal Chemistry," John Wiley and Sons, New York, N. Y., 1960.

(1) W. F. Luder, P. B. Kraus, C. A. Kraus, and R. M. Fuoss, *J. Am. Chem. Soc.*, **58**, 836 (1936).