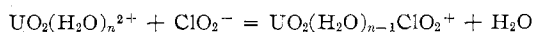


TABLE I
 $\text{UO}_2^{2+} \cdot \text{ClO}_2^-$ COMPLEX FORMATION IN PERCHLORIC ACID
 2-cm. cell at 25°, $I = 1.00 M$

$[\text{UO}_2^{2+}]$, M	ΣClO_2^- , M	$[\text{ClO}_2^-]$, M	$[\text{H}^+]$, M	A_{obsd}	$Q_{\text{370 m}\mu}$
0.20	0.00110	1.0×10^{-4}	0.10	0.214	0.535×10^4
0.179	0.004444	2.12×10^{-4}	0.200	0.379	0.499×10^4
0.00895	0.01386	2.97×10^{-3}	0.0367	0.264	0.497×10^4
0.04478	0.01386	4.14×10^{-4}	0.3253	0.187	0.504×10^4
0.1343	0.01386	1.53×10^{-3}	0.0806	1.980	0.482×10^4
0.04478	0.01386	2.03×10^{-3}	0.0582	0.969	0.533×10^4
0.0600	0.00560	2.67×10^{-4}	0.200	0.165	0.515×10^4
0.04478	0.01386	3.77×10^{-3}	0.0268	1.592	0.472×10^4

using the dissociation constant $K_a = 1.1 \times 10^{-2}$. The molar absorptancy, ϵ , is defined as $A = \epsilon l C$ 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



with an equilibrium constant Q where

$$Q = \frac{[\text{UO}_2 \cdot \text{ClO}_2^+]}{[\text{UO}_2^{2+}][\text{ClO}_2^-]}$$

the values of $Q\epsilon_\lambda$ can be evaluated at various wave lengths using the expression

$$Q\epsilon_\lambda = \frac{A_{\text{obsd}}/2}{[\text{UO}_2^{2+}][\text{ClO}_2^-]}$$

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 $Q\epsilon_\lambda$; however, Table I does contain all the data points for the limiting concentrations. The average value of $Q\epsilon_{370 \text{ m}\mu}$ from a series of 35 individual experiments was $0.497 \times 10^4 \pm 0.024 \times 10^4$. Additional values of $Q\epsilon_\lambda$ as a function of wave length were as follows: 300 m μ , 0.41×10^4 ; 340 m μ , 0.901×10^4 ; 390 m μ , 0.40×10^4 ; 410 m μ , 0.21×10^4 ; and 430 m μ , 0.11×10^4 .

The direct proportionality between the absorptancy 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 absorptancy, ϵ , 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 coefficients⁵ appear to be on the order of 10^4 – 10^5 . If this is used as an upper limit, using the data at 370 m μ , 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 $\text{UO}_2\text{ClO}_2^+$ complex is not a very stable species.

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A Crystalline Complex of Benzene and Tetrabutylammonium Perchlorate

BY R. P. SEWARD

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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 Fuoss¹ 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).

tion of dibutyl phthalate in benzene for several weeks were weighed and then decomposed by heating to 110°. The weight losses corresponded to 1.00–1.02 moles of benzene per mole of salt.

Cooling and heating curves on mixtures of benzene and tetrabutylammonium perchlorate of 70, 75, and 82% salt content showed a common thermal arrest at 62°. Above this temperature a rather viscous liquid phase remained at equilibrium with a white solid.

Decomposition pressures of the complex at 20.0, 25.0, and 31.0° were observed to be 16.2, 24.2, and 39.0 mm. with an uncertainty in the pressure measurements estimated to be $\pm 2\%$. These measurements were made with a mercury manometer connected to a high vacuum pump and, through a ground glass joint, to a small bulb in a constant temperature bath, which contained the compound. With a known weight of salt and benzene initially present, the composition of the system was determined from time to time by detaching and weighing the bulb. When the mole ratio of benzene to salt fell below 1.00 the equilibrium pressure remained constant while further benzene was pumped off.

The solubility of tetrabutylammonium perchlorate at 25° in water was found to be $0.0101 \pm 2\% m$ in the absence of benzene while in the three-phase system (benzene solution, water solution, crystalline complex) the concentration of salt in the aqueous phase was $0.0052 m$.

Discussion

The $0.0168 M$ concentration of tetrabutylammonium perchlorate at 25° in the upper layer of the unstable two liquid phase system is consistent with the solubility of $0.014 M$ in benzene at the freezing point of benzene as reported by Rothrock and Kraus.² In the earlier investigation crystallization of the complex had apparently never been initiated.

The weight loss experiments, and the observation that a constant equilibrium pressure was reached only when the benzene to salt mole ratio was below one, indicate a 1:1 mole ratio in the complex. As the complex is not very stable, losing benzene readily when exposed to the atmosphere at room temperature and melting incongruently at 72°, it presumably exists only in the crystalline state.

Standard state free energy increases accompanying the formation of the crystal complex from crystalline tetrabutylammonium perchlorate and liquid benzene have been calculated from the dissociation pressures at 20, 25, and 31° and benzene vapor pressures of 75.9, 95.2, and 124.8 mm. at these temperatures. Numerical values for ΔF° are -0.90 , -0.81 , and -0.70 kcal. mole⁻¹. From the variation of ΔF° with temperature, $\Delta H^\circ = -6.1$ kcal. mole⁻¹ and $\Delta S^\circ = -17.8$ cal. mole⁻¹ deg.⁻¹, independent of temperature within the limits of experimental precision.

The free energy of formation of the complex from liquid benzene and the solid salt may also be calculated from the solubility measurements. If the uncomplexed solid dissolves in the aqueous solution at $0.0101 m$, is then transferred to the aqueous phase saturated with benzene having $0.0052 m$ salt concentration, and the complex is crystallized from this solution, the free energy change is

$$\Delta F^\circ = RT \ln \frac{(0.0052)^2}{(0.0101)^2} = -0.78 \text{ kcal.}$$

(2) D. A. Rothrock and C. A. Kraus, *J. Am. Chem. Soc.*, **59**, 1699 (1937).

Any difference in the activity coefficient of the salt in the two solutions has been neglected here and the benzene vapor pressure of the aqueous phase when saturated with benzene assumed to be essentially that of pure benzene.

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Vapor Deposition of Pure Ruthenium Metal from Ruthenocene

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Biscyclopentadienyl metal compounds (metallocenes), because of their relatively high vapor pressure, may offer an attractive route to vapor deposition of metals, if used under the correct conditions. In previously reported studies, ferrocene decomposed to give hydrogen and diferrocenyl,¹ and other transition metal cyclopentadiene compounds gave deposits of metal carbide along with the metal.² However, a pure ruthenium metal film (99.99%) was deposited from bis(cyclopentadienyl)ruthenium at 595° in a hydrogen gas stream in the present work.

Experimental

Ruthenocene was prepared by the reaction of ruthenium trichloride with cyclopentadienylsodium in 1,2-dimethoxyethane.³ The crude product when sublimed *in vacuo* yielded a yellow crystalline solid with a sharp melting point of 199–200°.⁴

A small porcelain boat containing 1 g. of ruthenocene was placed in a 25 × 300 mm. Vycor tube fitted with an inlet and exit port (note Fig. 1). A cylindrical graphite susceptor (21 × 126 mm.), grooved to accommodate a sheathed thermocouple, was inserted in the Vycor tube approximately 3 in. from the porcelain boat. A small resistance furnace was positioned to heat the porcelain boat and contents. A radiofrequency induction heater coil outside the Vycor tube surrounded the graphite susceptor at a distance approximately 1 in. from the resistance heater. A flow of dry hydrogen (100 cc./min.) was passed through the Vycor tube *via* the inlet port. The ruthenocene was heated to 94° by the furnace while the induction heater was controlled so that the graphite susceptor temperature was maintained at 590–600° for approximately 2 hr. This arrangement was used to provide more accurate temperature measurement, but a separately controlled resistance furnace outside the tube could be used just as well. About 100 mg. of ruthenocene was consumed in the course of the run.

A metallic film, mirror-like in appearance and easily removable, formed on the wall of the Vycor tube immediately adjacent to the graphite susceptor. A nonuniform ruthenium metal deposit formed on the graphite susceptor. In contrast to the mirror-like film of the Vycor substrate, this metallic deposit was dull and light gray in appearance. The nonuniformity in the

(1) I. B. Johns, E. A. McElhill, and J. O. Smith, *J. Chem. Eng. Data*, **7**, 277 (1962).

(2) J. J. Bulloff, U. S. Patent 2,898,235 (Aug. 4, 1959).

(3) D. E. Bublitz, W. E. McEwen, and J. Kleinberg, *Org. Syn.*, **41**, 96 (1961).

(4) H. C. Kaufman, "Handbook of Organometallic Compounds," D. Van Nostrand Co., Inc., New York, N. Y., 1961, p. 1525.