Contribution from the Division of Mineral Chemistry,
CSIRO, Melbourne, Australia

Thermochemistry of Cyclopentadienylthallium

By H. HULL and A. G. TURNBULL

Received May 25, 1967

The standard heat of formation of $TlC_5H_5(c)$ was calculated to be 23.85 ± 0.6 kcal/mole from measurements of the heat of reaction of aqueous TlOH with gaseous C_5H_6 at 25°. The standard free energy of formation of $TlC_5H_5(c)$ was calculated to be 42.3 ± 0.5 kcal/mole from measurement of the pa_H of the above reaction at equilibrium at 25°. The standard entropy of $TlC_5H_5(c)$ was then calculated to be 38.3 ± 3 cal/deg mole. The different behavior of TlC_5H_5, $Fe(C_5H_5)_2$, and $Mg(C_5H_5)_2$ with respect to hydrolysis was shown to depend mainly on the free energies of formation of the metal hydroxides.

Introduction

Cyclopentadienylthallium, TlC_5H_5, is almost unique among cyclopentadienylmetal compounds in the fact that it may be prepared[1,2] from aqueous solution at room temperature

$$TlOH + C_5H_6(g) \rightleftharpoons TlC_5H_5(c) + H_2O \qquad (1)$$

The reaction is rapid and quantitative and TlC_5H_5 is almost insoluble in water, so that the process has been suggested for analytical use.[1] By contrast, the cyclopentadienyl compounds of the alkali and alkaline earths and manganese are hydrolyzed by water to give the hydroxides and C_5H_6.[3] Since thermochemical data were recently obtained[4] for $Mg(C_5H_5)_2$, it was thought that comparable data for TlC_5H_5 might help to explain the entirely different chemical behavior of the two compounds. It was found that the heat of formation of TlC_5H_5 could be readily obtained by measuring the heat of the preparation reaction itself. The method was simply to carry gaseous C_5H_6 in an argon stream into the calorimeter containing solution presaturated with TlC_5H_5, measure the heat of precipitation, and collect and weigh the solid TlC_5H_5 product. Adequate characterization of the product by analysis, density, and X-ray powder pattern was obtained.

The free energy of formation of TlC_5H_5 was also derived from measurements of the equilibrium $pa_H = -\log a_H$, where a_H is the hydrogen ion activity of the solution phase of reaction 1.

Experimental Section

Materials.—The TlOH stock solution was prepared by dissolving 20.00 g of AnalaR grade Tl_2SO_4 in 2100 g of distilled water and adding the solution slowly to 825 ml of 0.096 *N* carbonate-free $Ba(OH)_2$ to give stoichiometric precipitaton of $BaSO_4$. The TlOH solution was filtered off and stored over excess TlC_5H_5 in a polythene bottle, away from air and light, at 24 ± 1° for several weeks. The calculated concentration, based on Tl_2SO_4 used, was 0.596 wt % TlOH and analysis by the KIO_3 method[5] gave 0.595 ± 0.010 wt % TlOH. The solubility of TlC_5H_5 in this TlOH solution was found to be 0.022 wt % at 25° by weighing a sample of TlC_5H_5 before and after equilibration with solution. The C_5H_6 was prepared from Fluka dicyclopentadiene[6] and redistilled just before each run to avoid polymerization.

Method.—The calorimeter consisted of a gold-plated copper vessel of 600-cm³ capacity, separated by a 4-cm air gap from a water jacket held at 25.00 ± 0.01° by a thermistor controller. The vessel lid was sealed with a Teflon gasket and had openings for (a) a gold-plated brass stirrer in a Teflon bearing, (b) a gold well containing a Dymec Model 2850A quartz thermometer, (c) a gold well containing a heater made of 18.845-ohm Manganin wire wound on a threaded brass rod, and (d) a sintered-glass gas distributor. Complete details will be given elsewhere.[7]

For each experiment, 507.0 g of TlOH solution, saturated with TlC_5H_5, was filtered into the calorimeter vessel. After assembly, a flow of argon was passed *via* a coil of metal tubing into a presaturator containing TlOH solution in a water bath held at 25.00 ± 0.01° and then into the calorimeter *via* glass tubing. An electrical calibration was performed over the range 24.6–25.85° and the argon flow was then switched for 3 min to pass through a saturator containing freshly distilled C_5H_6 held at 25.00 ± 0.01°. After this the argon stream was continued to flush unreacted C_5H_6 from the calorimeter. The reaction period lasted 15–20 min, after which the rate of temperature drift returned to the expected value. A second calibration was then performed over the range 25.15–25.4° and agreed with the first within ±0.1%, the mean calorimeter constant being 600.5 cal/deg. The 0.5 g of C_5H_6 added to the calorimeter caused an increase in the calorimeter constant of only 0.2 cal/deg.

After each experiment, the precipitated TlC_5H_5 was rapidly collected on a sintered-glass filter, washed with TlC_5H_5-saturated water at 24 ± 1°, and dried in a vacuum desiccator over molecular sieves. No changes in appearance or weight were observed on storage in dry air in the dark. The degree of reaction, based on TlOH initially present, was 55–62%. The heat of reaction was calculated on the basis of the weight of TlC_5H_5 collected. Titrations of TlOH with standard KIO_3 before and after reaction gave comparable, but less accurate, results.

The product TlC_5H_5 was analyzed by the KIO_3 method. *Anal.* Calcd for TlC_5H_5: Tl, 75.85. Found: Tl, 76.18. It formed pale cream to fawn, diamond-shaped crystals of fairly uniform size (10–20 μ). The X-ray powder pattern showed only the lines expected from the reported monoclinic unit cell.[8] The density, determined on a sample of 0.7 g in a 10-ml water pycnometer, was 3.32 ± 0.03 g/cm³, in agreement with 3.33 g/cm³ measured on single crystals[8] and 3.37 g/cm³ calculated from the unit cell.[8]

Heats of reaction are given in Table I in terms of the thermochemical calorie (4.1840 joules) and based on the 1961 scale of atomic weights. The uncertainty is given as twice the standard deviation.

For equilibrium studies, 100 ml of the TlOH stock solution was

---

(1) H. Meister, *Angew. Chem.*, **69**, 533 (1957).

(2) F. A. Cotton and L. T. Reynolds, *J. Am. Chem. Soc.*, **80**, 269 (1958).

(3) G. Wilkinson, F. A. Cotton, and J. M. Birmingham, *J. Inorg. Nucl. Chem.*, **2**, 95 (1956).

(4) H. Hull, A. F. Reid, and A. G. Turnbull, *Inorg. Chem.*, **6**, 805 (1967).

(5) A. I. Vogel, "Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 1948.

(6) H. Hull, A. F. Reid, and A. G. Turnbull, *Australian J. Chem.*, **18**, 249 (1965).

(7) A. G. Turnbull, *J. Sci. Instr.*, in press.

(8) E. Frasson, E. Menegus, and C. Panattoni, *Nature*, **199**, 1087 (1963).

TABLE I

HEAT OF REACTION OF TlOH SOLUTION WITH C_5H_6 GAS AT 25°

ΔT, °C	q, cal	Wt of TlC_5H_5, g	ΔH, kcal/mole
0.2930	175.95	2.1570	−21.95
0.2682	161.0	2.0035	−21.65
0.2673	160.45	2.0682	−20.9
0.2720	163.4	2.0150	−21.85
0.2965	178.1	2.1400	−22.4
			Av −21.75 ± 0.5

placed in a polythene bottle in a water bath at 25.00 ± 0.01°. Argon was passed through a saturator, which was frequently replenished with freshly distilled C_5H_6 at 25°, and then into the solution through polythene tubing. The average partial pressure of C_5H_6 over the solution was 420 ± 20 mm, calculated from the known vapor pressure[6] and composition of slightly dimerized C_5H_6 in the saturator. A precipitate of pale yellow, well-crystallized TlC_5H_5 and a clear, pale yellow solution formed. The pa_H of the solution was measured to a precision of 0.01 unit using glass and calomel electrodes and a Pye pH meter. Standardization[9] was carried out using 0.01 m borax ($pa_H = 9.18$) and 0.025 m $NaHCO_3$–0.025 m Na_2CO_3 buffer ($pa_H = 10.00$). The solution pa_H fell from 12.35 to 10.0 ± 0.1 in 1 hr and remained constant. The solid TlC_5H_5 was then filtered off, washed, and added to distilled water through which C_5H_6-saturated argon was passed. The pa_H rose from 7.0 to 10.0 ± 0.1 in 1 hr and remained constant.

Results

Heat of Formation.—From the average concentrations of TlOH before and after reaction, the calorimeter process may be written

$$[\mathrm{TlOH}]_{\mathrm{TlOH:2050H_2O}} + C_5H_6(g) \longrightarrow TlC_5H_5(c) + [H_2O]_{\mathrm{TlOH:3550H_2O}} \quad (2)$$

The tabulated heat of formation data[10] for TlOH were extrapolated slightly (from 1:2000H₂O) to obtain $\Delta H_f{}^\circ{}_{298} = -54.49$ kcal/mole at 1:2050H₂O and $\Delta H_f{}^\circ{}_{298} = -54.56$ kcal/mole at 1:3550H₂O. The average value during reaction 2 was thus −54.53 ± 0.1 kcal/mole. The heat of formation of $C_5H_6(g)$ was recalculated recently[4] to be 31.82 ± 0.3 kcal/mole. The heat of formation of H_2O in TlOH:2800H₂O was derived from tabulated values[10] to be −68.32 ± 0.01 kcal/mole. Combining the above values with the heat of reaction 2 (from Table I), −21.75 ± 0.5 kcal/mole, gave $\Delta H_f{}^\circ{}_{298}[TlC_5H_5(c)] = 23.85 \pm 0.6$ kcal/mole.

Free Energy of Formation.—At equilibrium, reaction 1 may be written

$$\mathrm{TlOH}(a) + C_5H_6(\text{g, satd soln}) \rightleftharpoons TlC_5H_5(\text{c, satd soln}) + H_2O(a_w) \quad (3)$$

The system consisted essentially of three phases—gas (pure C_5H_6), liquid, and solid (pure TlC_5H_5)—and three components. Thus, fixing temperature and pressure gave unique activities of TlOH, TlC_5H_5, and C_5H_6 at equilibrium. The standard free energy of formation of dissociated TlOH in a standard state of ideal solution at unit molality is tabulated[10] as −45.33 kcal/mole. Thus for a solution of activity a

$$\Delta G_f{}^\circ{}_{298}[\mathrm{TlOH}] = -45.33 + RT \ln a \quad (4)$$

By definition, $a = a_{Tl^+}a_{OH^-}$ and by assumption, at the low concentration of 10^{-4} m involved, $a = a_{OH^-}{}^2$. Introducing the dissociation constant of water, K_w

$$\log a_{OH^-}{}^2 = \log (K_w/a_{H^+})^2$$
$$= 2(pa_H - 14.00) \quad (5)$$

Thus, using the observed pa_H of 10.0 ± 0.1 led to $\Delta G_f{}^\circ{}_{298}[\mathrm{TlOH}] = -56.24 \pm 0.3$ kcal/mole. It was considered that the uncertainty of ±0.1 in the pa_H value adequately covered any possible difference of liquid junction potentials[9] between standard buffers and TlOH solutions.

Furthermore, calculation by the Debye–Hückel method[10] gave a mean ionic activity coefficient of 0.99 for TlOH at $m = 10^{-4}$, so that the assumption $a_{Tl^+} = a_{OH^-}$ appeared adequate. The small concentrations of TlC_5H_5 and C_5H_6, estimated to be $\sim 10^{-3}$ and $\sim 10^{-2}$ m, respectively, would not influence the ionic activity coefficients appreciably.

The standard free energy of formation of C_5H_6 ideal gas at 1 atm pressure was previously calculated[11] to be 42.21 ± 0.3 kcal/mole, so that

$$\Delta G_f{}^\circ{}_{298}[C_5H_6] = 42.21 + RT \ln (p/760) \quad (6)$$

At the average pressure of 420 ± 20 mm, $\Delta G_f{}^\circ{}_{298}[C_5H_6] = 41.86 \pm 0.3$ kcal/mole. The activity of water in solution was effectively unity and the tabulated[10] value $\Delta G_f{}^\circ{}_{298}[H_2O(l)] = -56.69$ kcal/mole was used. Combining the above values and $\Delta G(2) = 0$ gave a value of $\Delta G_f{}^\circ{}_{298}[TlC_5H_5(c)] = 42.3 \pm 0.5$ kcal/mole.

Entropy.—Combining the standard heats and free energies of formation of TlC_5H_5 derived above gave $\Delta S_f{}^\circ{}_{298} = -61.9$ cal/deg mole and taking the tabulated[10] entropies of Tl(c), C(graphite), and $H_2(g)$ led to $S^\circ{}_{298}[TlC_5H_5(c)] = 38.3 \pm 3$ cal/deg mole.

This entropy may be compared with the measured value of 30.6 cal/deg mole for TlI.[12] The structure of TlC_5H_5 is reported[8] to be an infinite ionic lattice containing zigzag chains of $-Tl-C_5H_5-Tl-$ and is thus quite similar to the low-temperature form of TlI.[13] Owing to the similar size and weight of I and C_5H_5, the lattice vibrational entropy is expected to be similar in TlI and TlC_5H_5, but it is necessary to allow for the internal vibrations and free or restricted rotation of the C_5H_5 group. Calculation by the usual statistical mechanical methods using the 24 fundamental frequencies of C_5H_5 derived from spectral studies[14] on KC_5H_5 gave 3.8 cal/deg mole for the vibrational entropy and a maximum of 2.7 cal/deg mole for free rotation of C_5H_5. Thus the total estimated entropy of TlC_5H_5 is 37.1 cal/deg mole in reasonable agreement with the measured value of 38.4 ± 3 cal/deg mole.

---

[9] R. G. Bates, "Determination of pH," John Wiley and Sons, Inc., New York, N. Y., 1964.

[10] D. D. Wagman, W. H. Evans, I. Malow, V. B. Parker, S. M. Bailey, and R. H. Schumm, U. S. National Bureau of Standards Technical Note 270-2, U. S. Government Printing Office, Washington, D. C., 1966.

[11] A. G. Turnbull, *Australian J. Chem.*, in press.

[12] D. Cubicciotti, *J. Phys. Chem.*, **69**, 1410 (1965).

[13] G. Wykhoff, "Crystal Structures," Vol. I, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1965.

[14] P. Fritz, *Advan. Organometal. Chem.*, **1**, 239 (1964).

Discussion

With the data now available, summarized in Table II, the free energy change of the general "hydrolysis" reaction may be considered

$$M(C_5H_5)_n(c) + nH_2O(l) \rightleftharpoons M(OH)_n(c) + nC_5H_6(g) \quad (7)$$

where M = metal and n = metal valence. The free energy of formation of C_5H_6 ideal gas (1 atm pressure) is taken to be 42.2 kcal/mole[11] and that of water is −56.69 kcal/mole.[10]

Table II

Standard Free Energies of Formation at 25°, $\Delta G_f{}^\circ{}_{298}$, kcal/mole

TlC_5H_5(c)	42.3 ± 0.5	TlOH(c)	−46.8 ± 0.1[b]
$Fe(C_5H_5)_2$(c)	70.9 ± 1.5[a]	$Fe(OH)_2$(c)	−115.6 ± 1[c]
$Mg(C_5H_5)_2$(c)	53.1 ± 2[a]	$Mg(OH)_2$(c)	−199.3 ± 0.5[c]

[a] See ref 4. [b] See ref 10. [c] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, U. S. National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

For M = Tl, $\Delta G^\circ{}_{298}(7)$ = 9.8 kcal, in agreement with the observation that TlC_5H_5 is only very slightly hydrolyzed by water and may be made from TlOH and C_5H_6. Similarly for M = Fe, $\Delta G^\circ{}_{298}(7)$ = 11.3 kcal, so that $Fe(C_5H_5)_2$ is also resistant to hydrolysis as observed in practice.[3] The reaction between $Fe(OH)_2$(c) and C_5H_6, though possible in principle, is not observed in practice, probably owing to the extremely low solubilities of $Fe(OH)_2$ and $Fe(C_5H_5)_2$ in water.

For M = Mg, however, $\Delta G^\circ{}_{298}(7)$ = 54.6 kcal, in agreement with the observation[4] that $Mg(C_5H_5)_2$ undergoes rapid and quantitative hydrolysis. Consideration of Table II shows clearly that it is the relative free energies of the hydroxides which determine whether or not hydrolysis will occur. This effect overrides the smaller variations of free energy of the cyclopentadienyl–metal compounds. Previous workers[3] have proposed the hydrolysis reaction to distinguish between "ionic" and "covalent" cyclopentadienyl compounds. The present work shows that such a test reveals little about the type or strength of the cyclopentadienyl–metal bond. The hydrolysis of $Mg(C_5H_5)_2$ depends on the high affinity of Mg for oxygen, whereas the preparation of TlC_5H_5 in aqueous solution depends on the low affinity of Tl for oxygen and the solubility of TlOH in water.

Contribution from the Aerospace Research Laboratories, ARC, Wright-Patterson Air Force Base, Ohio 45433,
and the Department of Chemistry, Wright State University, Dayton, Ohio 45431

Determination of Rates of Optical Inversion of Aluminum β-Diketonate Complexes by Nuclear Magnetic Resonance Studies of Racemic Mixtures[1a]

By JOHN J. FORTMAN[1b] and ROBERT E. SIEVERS[1c]

Received May 24, 1967

Compounds of the form $Al(AA)_2(BB)$ and $Al(AA)(BB)_2$ can be prepared from $Al(AA)_3$ and $Al(BB)_3$, where AA and BB represent symmetrical bidentate ligands such as 2,2,6,6-tetramethyl-3,5-heptanedione [H(thd)], 2,4-pentanedione [H(acac)], and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione [H(hfa)]. Chlorobenzene solutions of these compounds in equilibrium with the parent tris species have been studied by nmr, and the equilibrium constants for the ligand exchange reactions measured at 25° are: $Al(acac)_3$ with $Al(thd)_3$, K = 1.5; $Al(hfa)_3$ with $Al(acac)_3$, $K = 3.34 \times 10^4$; and $Al(hfa)_3$ with $Al(thd)_3$, $K = 3.68 \times 10^4$. Large deviations from the statistical distribution of ligands (K = 9) were found. The mixed-ligand complexes are favored in both systems in which hfa is present while in the other equilibria the parent tris complexes are favored. The terminal groups of AA in complexes of the form $Al(AA)_2(BB)$ exhibit different resonances due to their structural nonequivalence; the two peaks coalesce as the temperature is raised. The coalescence is attributed to the optical inversion of the complex. The coalescence temperatures and rate constants of environmental averaging are: $Al(acac)_2(thd)$, 105°, 12.6 sec^{-1}; $Al(acac)(thd)_2$, 105°, 8.5 sec^{-1}; $Al(hfa)(thd)_2$, −8°, 6.9 sec^{-1}; and $Al(hfa)(acac)_2$, −18°, 5.3 sec^{-1}. Rates are determined for other temperatures, allowing the calculation of frequency factors and energies and entropies of activation. The rates were found to be independent of complex concentration and the presence of uncomplexed ligand, indicating an intramolecular racemization process. The relationship of the determined rates of environmental averaging to the rates of optical inversion are shown to be dependent on the mechanism of the process, and these relationships are discussed in detail for both bond rupture and nonbond rupture mechanisms. This technique permits the estimation of rates of racemization of complexes of the type $M(AA)_2(BB)$ without prior resolution of optical isomers.

Introduction

The great importance of nmr in structural studies of octahedral complexes of mixed bidentate ligand chelates was first demonstrated by Collman and co-workers[2] in 1962. Fay and Piper[3] have well established the value of nmr in estimating rates of geometrical isomerization of octahedral complexes with unsymmetrical bidentate ligands. Other systems have been examined in which

---

(1) (a) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967; (b) Wright State University; supported as a Visiting Research Associate, Ohio State Research Foundation; (c) Aerospace Research Laboratories.

(2) J. P. Collman, R. L. Marshall, and W. L. Young, III, *Chem. Ind.* (London), 1380 (1962).

(3) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964), and references cited therein.