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Free Energies of Formation of Metal–TCNQ Anion Radical Salts

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Free energies of formation were determined for the TCNQ anion radical salts of Li, Na, K, Ba, Ag, Cu, Ni, and Pb. Aqueous electrochemical cell measurements at room temperature were used. The results are qualitatively similar to data on the corresponding metal iodides.

Introduction

Many studies have been made on the salts of 7,7,8,8-tetracyanoquinodimethan (TCNQ) since their discovery by Acker *et al.* (*1*) in 1960. Electrical, optical, and magnetic properties, phase equilibria, and crystal structures have been investigated (*2*). There has been relatively little work on the heats and free energies of formation of TCNQ Salts. Boyd (*3*) determined the heats of formation of TCNQ, NH_4TCNQ, and organic salts of TCNQ from heat of combustion measurements. Metzger (*4*) performed Madelung energy calculations on NaTCNQ, RbTCNQ, and NH_4TCNQ. He concluded that this type of calculation does not account for a large fraction of the binding energy.

In the present investigation, aqueous electrochemical cell measurements at room temperature were made on the TCNQ salts of Li, Na, K, Ba, Ag, Cu, Ni, and Pb. Free energies of formation were calculated from the data.

Experimental

7,7,8,8-Tetracyanoquinodimethan, 98% pure, was obtained from the Aldrich Chemical Co. of Milwaukee, Wisconsin. It was recrystallized from acetonitrile prior to use. The metal-TCNQ salts were prepared by the methods of Melby *et al.* (*5*). Metal analyses on the salts were performed by Schwarzkopf Microanalytical Laboratory of Woodside, N.Y.. The weight percent metal found and the theoretical weight percent (in parentheses) were Li, 3.2 (3.3); Na, 10.1 (10.1); K, 15.6 (16.1); Ba, 24.5 (25.2); Ag, 33.8 (34.6); Cu, 13.1 (13.5); Ni, 11.1 (11.3); Pb, 30.9 (32.2). The analytical values correspond approximately to those found by Melby *et al.* (*5*). Analysis for lithium was performed on the salts of Ag, Cu, Pb, and Ni which were prepared by reaction with LiTCNQ (*5*). The amount of Li was found to be less than 0.01 wt% in each use.

The electrochemical measurements were made in a Pyrex H-tube in which the two half-cells were separated by a fine-frit Py-

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rex disc. During each run, nitrogen gas was bubbled slowly through the solution in each half-cell to avoid contamination by oxygen. Two types of cell were used. The cell reaction in the first three cells listed in Table I produces only the anion radical salt. For example, the virtual cell reaction for the third cell in Table I is

$$\mathrm{Pb} + 2\mathrm{TCNQ} + 1.5\mathrm{H_2O} = \mathrm{Pb(TCNQ)_2} \cdot 1.5\mathrm{H_2O} \quad (1)$$

An example of the virtual cell reactions for the other six cells in Table I is that for the fourth cell

$$2\mathrm{Hg} + \mathrm{NiCl_2}(0.01\ M) + 2\mathrm{TCNQ} + 3\mathrm{H_2O} = \mathrm{Hg_2CL_2} + \mathrm{Ni(TCNQ)_2} \cdot 3\mathrm{H_2O} \quad (2)$$

In the case of the potassium salt, two different electrolytic solutions were used for comparison purposes, 0.01 *M* KCl and a saturated KCl solution.

Experimental data were obtained on a number of these cells at temperatures between 25 and 65°C in an attempt to determine the temperature dependence of the emf. The changes in emf with temperature were generally small (1 to 2 mV/10°C). However, the experimental scatter of the data was too great to permit accurate determination of the temperature dependence. Therefore, data at 25°C only are reported. The limits of error for the emf listed in Table I are estimated from the variation in emf observed in a single run at 25°C and from a comparison of data obtained in two or more runs on different cells containing the same materials. In runs in which the temperature was raised to 65°C over a period of several hours and then brought back down to 25°C, the variation of emf at 25°C within a run could be greater than the limits listed in Table I.

To determine the free energies of formation of the TCNQ salts from the cell reactions of the type shown in Reaction (2), free energy data on the salts Hg_2Cl_2, $NiCl_2$, LiCl, NaCl, KCl, and $BaCl_2$ were used (*6*). Mean ionic activity coefficients for these aqueous salts (*7*) were also employed in the calculations.

Results and Discussion

The emf data in Table I were used to calculate free energies of formation of the metal–TCNQ salts. The free energy values are shown in the second column of Table II. The error in the free energy values based on the spread of the emf data in Table I is much smaller than ±1 kcal/mole metal.

TABLE I

ELECTROCHEMICAL CELLS FOR DETERMINING FREE ENERGIES OF FORMATION OF METAL–TCNQ SALTS AT ROOM TEMPERATURE

Electrochemical cell[a]	Cell voltage (mV)
$\mathrm{Ag}\vert\mathrm{AgNO_3}(0.1\ M)\vert\mathrm{AgTCNQ,TCNQ,Pt}$	106 ± 5
$\mathrm{Cu}\vert\mathrm{CuSO_4}(0.1\ M)\vert\mathrm{Cu(TCNQ)_2,TCNQ,Pt}$	276 ± 15
$\mathrm{Pb}\vert\mathrm{Pb(NO_3)_2}(0.1\ M)\vert\mathrm{Pb(TCNQ)_2} \cdot 1.5\mathrm{H_2O,TCNQ,Pt}$	512 ± 17
$\mathrm{Hg,Hg_2Cl_2}\vert\mathrm{NiCl_2}(0.01\ M)\vert\mathrm{Ni(TCNQ)_2} \cdot 3\mathrm{H_2O,TCNQ,Pt}$	3 ± 6
$\mathrm{Hg,Hg_2Cl_2}\vert\mathrm{LiCl}(0.01\ M)\vert\mathrm{LiTCNQ,TCNQ,Pt}$	−218 ± 8
$\mathrm{Hg,Hg_2Cl_2}\vert\mathrm{NaCl}(0.01\ M)\vert\mathrm{NaTCNQ,TCNQ,Pt}$	−65 ± 10
$\mathrm{Hg,Hg_2Cl_2}\vert\mathrm{KCl}(0.01\ M)\vert\mathrm{KTCNQ,TCNQ,Pt}$	−75 ± 8
$\mathrm{Hg,Hg_2Cl_2}\vert\mathrm{KCl(sat.)}\vert\mathrm{KTCNQ,TCNQ,Pt}$	202 ± 11
$\mathrm{Hg,Hg_2Cl_2}\vert\mathrm{BaCl_2}(0.01\ M)\vert\mathrm{Ba(TCNQ)_2,TCNQ,Pt}$	−55 ± 6

[a] Anode (oxidation) is on the left when the cell voltage is positive.

TABLE II

FREE ENERGIES OF FORMATION OF METAL–TCNQ SALTS

Reaction	$-\Delta G^\circ_{298^\circ K}$[a] (kcal/mole metal)	$-\Delta H^\circ_{f298^\circ K}$ corresponding metal iodide[b] (kcal/mole metal)
Ag + TCNQ = AgTCNQ	2.4	14.9
Cu + 2TCNQ = $Cu(TCNQ)_2$	13.5	1.7
Pb + 2TCNQ + $1.5H_2O$ = $Pb(TCNQ)_2 \cdot 1.5H_2O$	23.6	41.9[c]
Ni + 2TCNQ + $3H_2O$ = $Ni(TCNQ)_2 \cdot 3H_2O$	31.6	20.5[c]
Li + TCNQ = LiTCNQ	76.9	64.8
Na + TCNQ = NaTCNQ	72.8	68.8
K + TCNQ = KTCNQ	77.5 77.1[d]	78.3
Ba + 2TCNQ = $Ba(TCNQ)_2$	152.1	144.0
$0.5N_2(g) + 2H_2(g)$ + TCNQ = NH_4TCNQ	55.7[e]	48.3

[a] These free energy values are for the chemical reactions on the left.
[b] Heats of formation from Ref. (*6*).
[c] Heats of formation of anhydrous iodides.
[d] Value obtained from cell with saturated KCl.
[e] Enthalpy change for reaction on the left obtained from Ref. (*3*).

However, since indeterminate experimental errors may effect the accuracy of the data and since some error is present in the literature values used in the calculations, we estimate an error in the ΔG° values of ±2 kcal/mole metal.

There are few data available with which to compare the free energy values in Table II. Since the reactants and products are, with the exception of water, all solids, the entropy of reaction is small. The difference between the enthalpy and free energy of reaction is, probably, not more than 1–2 kcal/mole metal. Since more enthalpy than free energy data are available, comparison of the free energy data in the second column of Table II will be made with enthalpy data from other sources.

Metzger (*4*) has presented the difficulties in attempting to determine the enthalpies of formation of the TCNQ salts from theoretical calculations. Metzger has estimated an enthalpy of formation of NaTCNQ using the data of Boyd (*3*) on NH_4TCNQ and making the crude assumption that the enthalpy of formation of NH_4TCNQ and NaTCNQ differ only because of the difference in the enthalpies of formation of $NH_4^+(g)$ and $Na^+(g)$. His value for the enthalpy of the reaction in Table II leading to the formation of NaTCNQ is -59.5 kcal/mole metal. This value is within range of the corresponding free energy value in Table II, -72.8 kcal/mole metal.

It is useful to make a qualitative comparison between the free energies of formation of the TCNQ salts and the enthalpies of formation of the corresponding metal iodides. Both elemental iodine and TCNQ are solid reactants. Unlike TCNQ, however, iodine dissociates to form the salt. The suggestion that the enthalpies of formation of the TCNQ salts and the corresponding iodides are similar is supported by a comparison of the data on NH_4TCNQ and NH_4I. This comparison is shown in the last row in Table II. The value for NH_4TCNQ, -55.7 kcal/mole, is fairly close to the value for NH_4I, -48.3 kcal/mole. The free energy values for the barium and alkali metal salts of TCNQ are similar to the enthalpy values for the corresponding iodides. This similarity supports the hypothesis that chemical bonding in these TCNQ salts, like the iodides, is primarily ionic.

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