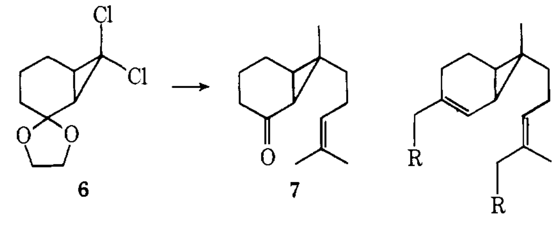

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8, R = H
9, R = OH

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(7) The reaction of **3** with lithium dimethylcuprate and lithium divinylcuprate proceeded similarly, whereas the one with lithium di-*n*-butylcuprate was apparently different. When 1,1-dibromo-2-phenylcyclopropane was treated with lithium dimethylcuprate in the absence of methyl iodide (−38° to 0°, 3 h, quenching with H_2O), a mixture of *rac*-1-bromo-1-methyl-*tert*-2-phenylcyclopropane and its diastereomer (57:43 ratio, 49% yield) was obtained besides a small amount of 1,1-dimethyl-2-phenylcyclopropane (17%). The reaction with lithium divinylcuprate (−78° to −70°, 1 h, quenching with MeI) also gave a mixture of *rac*-1-bromo-1-vinyl-*tert*-2-phenylcyclopropane and its diastereomer (72:28 ratio, 69% yield). In sharp contrast, however, no trace of 1-bromo-1-*n*-butyl-2-phenylcyclopropane was obtained in the reaction of 1,1-dibromo-2-phenylcyclopropane with lithium di-*n*-butylcuprate (entry 1, 2). Clearly, either bromine–methyl or bromine–vinyl exchange is predominant in the former cases over the preferred bromine–copper exchange in the lithium di-*n*-butylcuprate reaction.

(8) 1,1-Dibromo-2-phenylcyclopropane was treated with lithium di-*n*-butylcuprate (prepared at −48°) at −78°, and the reaction mixture was gradually warmed. Quenching the mixture with methanol at −48, −21, and −10° resulted in the formation of 1-butyl-2-phenylcyclopropane with 19:81 cis/trans ratio. This indicates that the species such as **2** is, at least, configurationally stable at the temperature examined.

(9) The addition of *n*-Bu_3P also decreased the stereoselectivity.

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(12) The lithium reagent was prepared from the corresponding bromide and lithium dispersion containing ca. 5% sodium metal in ether at −10°. Cuprates prepared from Grignard reagents were tried without success. The C–MgX to C–Cu conversion requires the use of equimolar *n*-Bu_3P, which has, however, been found to be detrimental to the reaction of dihalocyclopropanes.

(13) The compound was obtained by dichlorocarbene addition (phase-transfer technique) to cyclohexenone ethylene acetal (71% yield) (ir (neat): 1107, 1020, 948,784 cm^{-1}; bp 88–90 °C/(1 mm)). Anal. Calcd for $C_9H_{12}O_2Cl_2$: C, 48.45; H, 5.42. Found: C, 48.70; H, 5.72.

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Determination of Gibbs Energies for Solid–Solid Phase Transitions in Electrochemical Double Cells without Liquid Junction: Calcite, Aragonite, and Vaterite

Sir:

We have developed a novel electrochemical method for the study of solid–solid phase transitions of metal salts. The method involves the use of electrochemical double cells without liquid junction for which the solid–solid phase transition of interest is the net cell reaction. We report here the use of the method for the determination of the Gibbs energy of transformation for the aragonite-to-calcite and vaterite-to-calcite phase transformations of $CaCO_3$. The aragonite–calcite phase transition is of special interest because of its potential use as a geobarometer,[1] and vaterite, aragonite, and calcite are found in the shells of various marine organisms.[2] Calcite is hexagonal with a density of 2.710 g cm^{-3} and a primary coordination of 9; aragonite is orthorhombic with a density of 2.944 and a primary coordination of 6; and, vaterite is pseudo-hexagonal with a density of 2.66 [3,4] Aragonite is a high pressure form of $CaCO_3$, whereas vaterite is apparently metastable with respect to calcite and aragonite at 25 °C. The phase transformations are sluggish around room temperature and thermodynamic data for the transitions around 25 °C have been obtained primarily by indirect methods.

We have investigated the aragonite–calcite phase transition in the double cell

$$\begin{aligned}&\mathrm{Pb(Hg,\ two\text{-}phase)|PbCO_3(s),\ CaCO_3(aragonite)|}\\ &\qquad\mathrm{CaCl_2(aq,\ m_1)|Hg_2Cl_2(s)|Hg(l)||}\\ &\qquad\mathrm{Hg(l)|Hg_2Cl_2(s)|CaCl_2(aq,\ m_1)|}\\ &\qquad\mathrm{CaCO_3(calcite),\ PbCO_3(s)|Pb(Hg,\ two\text{-}phase)}\qquad(1)\end{aligned}$$

The cell reaction for the left half of the double cell is

$$\begin{aligned}&\mathrm{Pb(Hg) + CaCO_3(aragonite) + Hg_2Cl_2(s)}\\ &\qquad= \mathrm{PbCO_3(s) + CaCl_2(aq,\ m_1) + 2Hg(l)}\qquad(2)\end{aligned}$$

whereas for the right half of the cell we have

$$\begin{aligned}&\mathrm{2Hg(l) + CaCl_2(aq,\ m_1) + PbCO_3(s)}\\ &\qquad= \mathrm{Hg_2Cl_2(s) + CaCO_3(calcite) + Pb(Hg)}\qquad(3)\end{aligned}$$

If we use the same $CaCl_2(aq)$ solution in both halves of the double cell, then the sum of reactions 2 and 3 yields for the net reaction of the double cell

$$\mathrm{CaCO_3(aragonite) = CaCO_3(calcite)}\qquad(4)$$

A cell analogous to (1) but with vaterite in place of aragonite has the net cell reaction

$$\mathrm{CaCO_3(vaterite) = CaCO_3(calcite)}\qquad(5)$$

For the net reactions given above $E_{\mathrm{cell}} = E_{\mathrm{tr}}{}^\circ$, and thus $\Delta\bar{G}_{\mathrm{tr}}{}^\circ = -2FE_{\mathrm{tr}}{}^\circ$; the voltage of the double cell should be independent of the $CaCl_2(aq)$ concentrations. The double-cell technique yields $\Delta\bar{G}_{\mathrm{tr}}{}^\circ$ directly, rather than as a small difference between two large numbers. Also, the double cell separates the two $CaCO_3$ phases such that crystals of the more stable phase are not in contact with the same cell electrolyte as those of the less stable phase, and therefore cannot catalyze the phase transformation of the less stable form.

Because of the sensitivity of the two-phase lead amalgam (~5 wt % Pb) to oxygen, the entire cell was set up on the high vacuum line; all cell components were introduced to the cell under oxygen-free conditions.[5] The $Pb(Hg)|PbCO_3(s)$, $CaCO_3(s)|Ca^{2+}(aq)$, and $Hg(l)|Hg_2Cl_2(s)|Cl^-(aq)$ electrodes were prepared as recommended in the literature.[6,7] The calcite used in the cells was prepared from primary standard $CaCO_3(s)$ which was covered with distilled water and held at 80 °C for several days. Synthetic aragonite was prepared according to the method described by Wray and Daniels.[8] Synthetic vaterite was prepared according to Turnbull's[4] method A1, except that the aging time was cut to 18 min; the sample was washed five times with distilled water and five times with absolute ethanol and then dried with an aspirator. The vaterite, aragonite, and calcite samples were authenticated by x-ray powder patterns and by the scanning electron microscope. Electron microprobe analysis showed that there were no impurities at the 0.01% level in our synthetic samples. All other chemicals used were reagent grade.

Emf measurements at 22 ± 1 °C on cells of the type (1) at

$CaCl_2$(aq) concentrations of 1, 5, and 10 mM gave the following E values: 7.16 ± 0.04, 7.06 ± 0.11, and 7.21 ± 0.14 mV, respectively. These are the average values of the cell voltages over a 3-day period. The uncertainties are the standard deviations. The absence of hysteresis in current–voltage plots provided strong evidence that the cells were operating reversibly. The cells 5 and 10 mM in $CaCl_2$(aq) were also 0.4 mM in $MgCl_2$, because Mg^{2+} was reported[9] to inhibit the aragonite-to-calcite transformation. Analogous emf measurements on cells of the type (1) but with vaterite in place of aragonite gave the following E values: 19.01 ± 0.30 mV [1 mM $CaCl_2$(aq)] and 19.21 ± 0.14 mV [5 mM $CaCl_2$(aq) + 0.4 mM $MgCl_2$(aq)] over a 3-day period at 22 ± 1 °C. The above data yield for the aragonite-to-calcite transition at 22 °C, E_{tr}° = 7.14 ± 0.18 mV and $\Delta\bar{G}_{\mathrm{tr}}^\circ = -330 \pm 8$ cal mol^{-1}, whereas for the vaterite-to-calcite transition we compute E_{tr}° = 19.11 ± 0.33 mV and $\Delta\bar{G}_{\mathrm{tr}}^\circ = -881 \pm 15$ cal mol^{-1}. Since $\Delta\bar{V} = 2.936$ cm^3 mol^{-1} for the aragonite-to-calcite transition, we compute that the pressure at which aragonite and calcite are in equilibrium at 22 °C is 4.6 ± 0.1 kbar (the effect due to compressibility is negligible). Since $\Delta\bar{V} = -0.69$ cm^3 mol^{-1} for the vaterite-to-calcite transition, equilibrium is not possible between vaterite and calcite around room temperature, as noted by Turnbull.[4]

Data at 25 °C on aragonite and calcite from ref 10 yield $\Delta\bar{G}_{\mathrm{tr}}^\circ = -250$ cal mol^{-1}, $\Delta\bar{H}_{\mathrm{tr}}^\circ = 50$ cal mol^{-1}, and $\Delta\bar{S}_{\mathrm{tr}}^\circ$ = 1.0 cal K^{-1} mol^{-1} (no error limits given for these quantities and no data given on vaterite). Kelley and Anderson report[11] $\Delta\bar{G}_{\mathrm{tr}}^\circ = -273$ cal mol^{-1}, $\Delta\bar{H}_{\mathrm{tr}}^\circ = 42$ cal mol^{-1}, and $\Delta\bar{S}_{\mathrm{tr}}^\circ$ = 1.06 cal K^{-1} mol^{-1} at 25 °C. Buchan[12] reported $\Delta\bar{G}_{\mathrm{tr}}^\circ = -414$ ± 9 (25 °C) from measurements on cells with liquid junction, but his reported cell stability was poor (~5 min). Kobayashi,[13] on the basis of heat capacity measurements, reported $\Delta\bar{G}_{\mathrm{tr}}^\circ = -311 \pm 23$ cal mol^{-1} (25 °C), in excellent agreement with our results. The ratio of the K_{sp} values at 25 °C for aragonite and calcite reported by Christ et al.[14] yield $\Delta\bar{G}_{\mathrm{tr}}^\circ = -218 \pm$ 109 cal mol^{-1}, which is marginally consistent with our value of -330 ± 8 cal mol^{-1}. Values of the aragonite–calcite transition pressure are exceedingly difficult to determine directly around room temperature. Our calculated value of 4.6 ± 0.1 kbar is consistent with several values obtained by extrapolation of high temperature data,[15-19] namely, 3-5 kbar. On the basis of conductivity measurements of saturated aqueous solutions at high pressure Jamieson[20] reported P_{tr} = 3.8 kbar at 25 °C. From the results of extensive heat capacity measurements, Staveley and Linford[21] obtained $\Delta\bar{S}_{\mathrm{tr}}^\circ = 0.89 \pm 0.05$ cal K^{-1} mol^{-1} at 25 °C. Combination of our $\Delta\bar{G}_{\mathrm{tr}}^\circ$ value with $\Delta\bar{S}_{\mathrm{tr}}^\circ$ = 0.89 yields $\Delta\bar{H}_{\mathrm{tr}}^\circ = -65 \pm 23$, which is in disagreement with the $\Delta\bar{H}_{\mathrm{tr}}^\circ$ values of Bäckström[22] (30 ± 20 cal mol^{-1} at 25 °C) and Roth and Chall[23] (48 cal mol^{-1} at 50 °C), obtained from heats-of-solution measurements. A possible source for this discrepancy can be found in the study of Rao et al.[24] on the effect of impurities on $\Delta\bar{H}_{\mathrm{tr}}^\circ$. They found that at 480 °C $\Delta\bar{H}_{\mathrm{tr}}^\circ$ increased from about 45 cal mol^{-1} for high purity aragonite and calcite to 230 cal mol^{-1} as the Sr^{2+} content was increased from >0.001 to 1%. The Sr^{2+} content in our samples was <0.005% (electron microprobe). Combination of Rao's $\Delta\bar{H}_{\mathrm{tr}}^\circ$ = 45 ± 10 cal mol^{-1} (480 °C) with Kobayashi's[13] heat capacity data yields $\Delta\bar{H}_{\mathrm{tr}}^\circ = -85 \pm 30$ cal mol^{-1} mol at 25 °C. Because $\Delta\bar{S}_{\mathrm{tr}}^\circ$ is positive, a negative value of $\Delta\bar{H}_{\mathrm{tr}}^\circ$ implies that aragonite and calcite cannot exist in equilibrium at 1 atm.

On the basis of solubility measurements on vaterite and calcite, Turnbull has reported[4] a value of $\Delta\bar{G}_{\mathrm{tr}}^\circ = -790 \pm 25$ cal mol^{-1} for the vaterite-to-calcite transition. This result is in reasonable agreement with our directly measured value of -881 ± 15 cal mol^{-1}.

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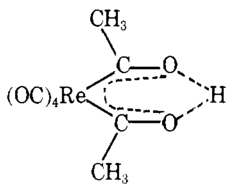
Reactions of Coordinated Molecules. V. Preparation of *cis*-$(OC)_4Re[C(CH_3)O\cdots H\cdots OC(CH_3)]$: the Enol Tautomer of a Metalloacetylacetone Molecule

Sir:

In a previous communication,[1] we reported the preparation of the first example of a "metalloacetylacetonate" anion and the complexation of this anion to a central aluminum ion forming a neutral tris-chelate complex. We now wish to report the preparation of the neutral molecule obtained from the protonation of a "metallo(acac)" anion. This molecule, **1**, is the metallo analogue of the enol tautomer of acetylacetone (**2**), where the methine group of **2** is replaced formally by the $Re(CO)_4$ group.



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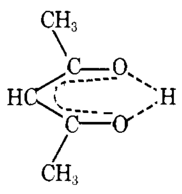

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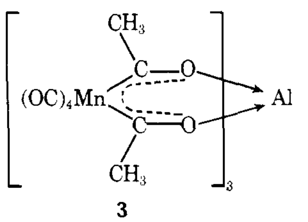

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