While a true comparison should only be made in the vapor state, it is highly improbable that a difference of 9.5 kcal. will be found in the heats of vaporization of this pair of isomeric glycerides.

It is believed that for the solid monoglycerides the heat of combustion will change in a regular fashion with the length of the carbon chain of the substituted fatty acid. Rossini[12] has reported for the gaseous saturated normal hydrocarbons a difference in the heat of combustion per CH_2 group of 157.00 ± 0.08 kcal. per mole. Since the glycerides are composed of a compact head (the glycerol) and a long tail (the fatty acid chain), the possibility is good that the head of the molecule will have little effect on the heat of combustion value upon changing the length of the fatty acid chain by several CH_2 groups. If this is true, α-monomyristin (the fatty acid is two CH_2 groups shorter in chain length than the palmitic acid) would have a calculated heat of combustion of 2464.78 ± 0.36 kcal. per mole. The preliminary values listed below for α-monomyristin give for the heat of combustion 2464.32 ± 0.59 kcal. per mole.

Mean value, $-\Delta U_{B/M} = 8152.1 \pm 1.9$ cal. g.$^{-1}$ (4 combustions, one sample)
Precision error = ±0.024%
Density = 1.01 g. cc.$^{-1}$
$C_p = 0.436 \pm 0.001$ cal. g. deg.$^{-1}$
$-\Delta U_B = 2465.56 \pm 0.59$ kcal. mole^{-1}
$-\Delta U_R = 2464.32 \pm 0.59$ kcal. mole^{-1}

Investigations are now under way to determine how far such values can be calculated without exceeding the limits of error on the experimental determinations and will be reported in future publications.

Acknowledgment.—The samples used throughout this investigation were prepared through the kindness of Bernard F. Daubert of the School of Pharmacy, Herbert E. Longenecker and R. R. Musulin of the Department of Chemistry, University of Pittsburgh. The authors also wish to acknowledge the many helpful suggestions made by C. G. King of the Department of Chemistry of the University of Pittsburgh.

Summary

1. The heats of combustion of α- and β-monopalmitin reduced to the standard state, $-\Delta U_R$, are reported as 2778.78 ± 0.36 and 2788.30 ± 0.67 kcal. per mole for the reaction carried out at one atmosphere pressure and 25°.

2. The difference in the heats of formation or the heat of the shift of the β form to the α form of −9.52 kcal. per mole is in agreement with the chemical behavior of the isomers but is larger in magnitude than had been expected.

3. As necessary auxiliary measurements, the approximate densities and the heat capacities at 25° of α- and β-monopalmitin are reported.

PITTSBURGH, PENNA. RECEIVED MAY 6, 1940

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[12] Rossini, *Ind. and Eng. Chem.*, **29**, 1425 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Silver–Silver Iodide Electrode

BY ROBERT K. GOULD AND W. C. VOSBURGH

The two most recent determinations of the normal potential of the silver–silver iodide electrode by Owen[1] and Cann and Taylor[2] led to the values 0.1522 v. and 0.1510 v., respectively. Because of the disagreement, a new determination was undertaken by the method used by Owen, but with an acetate instead of a borate buffer. The cell measured was

$$H_2/HAc(m_1),\ NaAc(m_2),\ KI(m_3)/AgI,\ Ag$$

in which m_1, m_2 and m_3 were all either about 0.01 m or between 0.004 and 0.005 m.

Experimental

Potassium iodide was twice recrystallized as described by Owen[1] and dried at 110°. Potentiometric titration of the iodide by a permanganate solution standardized against arsenious oxide[3] showed it to be pure within the error of the analysis, which was about one part in a thousand.

A 0.1 N sodium hydroxide solution was standardized against potassium acid phthalate from the National Bureau of Standards. A 0.1 N acetic acid solution was carefully standardized against the sodium hydroxide solution. Portions of the acid solution containing either 0.02 or 0.01 mole of the acid were half neutralized with the sodium hydroxide solution; then either 0.01 or 0.004 mole of potassium iodide and enough water to make 1000 g. of

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[1] Owen, THIS JOURNAL, **57**, 1526 (1935).

[2] Cann and Taylor, *ibid.*, **59**, 1484 (1937).

[3] Kolthoff, Laitinen and Lingane, *ibid.*, **59**, 430 (1937).

TABLE I

CELL $H_2/HAc(m_1)$, $NaAc(m_2)$, $KI(m_3)/AgI$, Ag AT 25°

Group no.	No. of cells	HAc $m_1 \times 10^3$	NaAc $m_2 \times 10^3$	KI $m_3 \times 10^3$	E_{25} v.	Av. dev., mv.	$E^{0\prime}_{25}$ v.
1	4	4.607	4.505	4.275	0.26934	0.065	−0.15181
2	2	10.000	9.992	10.257	.24744	.005	− .15166
3	2	10.021	10.003	10.341	.24715	.015	− .15171
4	5	10.040	9.954	10.241	.24719	.01	− .15175

solvent were added. Dissolved air was displaced by a stream of purified nitrogen and the solutions were used for the cell electrolytes.

Silver–silver iodide electrodes were prepared by the thermal method[4] from a paste of silver oxide and silver iodide, which was heated at about 475°. These electrodes were found more reproducible than electrodes made from silver iodate and oxide by heating at 600°.

Cell vessels of the type shown in Fig. 1 were used, with the hydrogen electrode in A and the silver–silver iodide electrode in B. When the cell was prepared, the portion of the connecting tube just below stopcock C was left unfilled with solution. Previous to a measurement, this tube was filled with solution from the horizontal reservoir by suction through the three-way stopcock C. After a measurement, the liquid connection between the two electrodes was broken by drawing some solution through stopcock D with hydrogen entering through stopcock C to replace it.

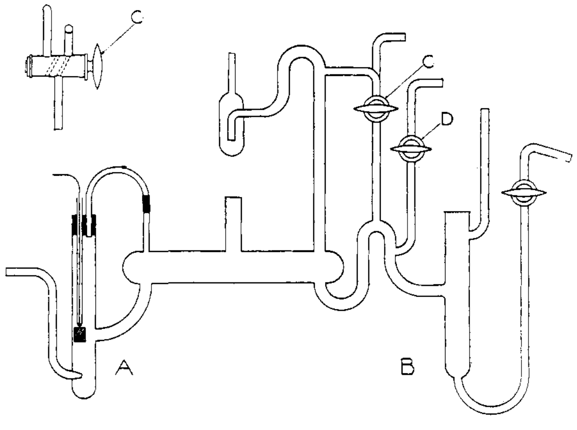

Fig. 1.—Cell vessel.

In the preparation of a silver–silver iodide electrode system, the dry electrode was put in place in part B of the vessel and the vessel alternately evacuated and filled with dry nitrogen three times. It was finally evacuated for fifteen minutes before the oxygen-free electrolyte solution was allowed to enter the vessel. The system was allowed to stand overnight with the solution in the vessel. In the morning the solution in B was drawn out, being replaced temporarily by nitrogen, and then solution from the horizontal reservoir drawn in. A platinized platinum electrode prepared as described by Popoff, Kunz and Snow[5] was inserted in A of Fig. 1, the vessel placed in a water-bath at 25 ± 0.02° and electrolytic hydrogen purified by passage first over solid potassium hydroxide and then over copper at 400 to 500° passed in.

Electromotive force measurements were made by means of a Leeds and Northrup Type K potentiometer and the standard cells previously described.[6] The electromotive forces usually became constant within two hours. Some of the cells were measured at other temperatures after the attainment of constancy at 25°. Five cells were measured at 25, 30, 35, 40 and again at 25°. Four cells were measured at 25, 20, 15, 10 and again at 25°. In Table I are given the compositions of the electrolytes and the electromotive forces at 25° corrected to one atmosphere of hydrogen.

The normal electrode potential, E^0, was calculated by means of the equation[7]

$$E - E^0 + k \log \frac{m_{\mathrm{HAc}} m_{\mathrm{I}}}{m_{\mathrm{Ac}}} = -k \log \frac{\gamma_{\mathrm{H}}\gamma_{\mathrm{I}}\gamma_{\mathrm{HAc}}}{\gamma_{\mathrm{H}}\gamma_{\mathrm{Ac}}} - k \log K \quad (1)$$

in which k stands for $2.303\ RT/F$, m_{HAc} and m_{Ac} are the molalities of undissociated acetic acid and of acetate ion, respectively, calculated from m_1 and m_2 of Table I, and K is the ionization constant of acetic acid. For the latter, the values of Harned and Ehlers were used. The values of $E^{0\prime}$ in Table I were calculated with neglect of the activity coefficient term. The small difference between the value for Group 1 and other values was attributed to the neglect of the activity coefficient term, and a linear extrapolation to zero ionic strength made by plotting $E^{0\prime}$ against ionic strength. The value of E^0_{25} so found was −0.15188 v. Calculation of E^0 from equation 1 with the use of activity coefficients from Kielland's table[8] gave −0.15189 v. for group 1 and −0.1520 v. for the average of the other cells. The latter is the less certain and probably too high because of uncertainty in the activity coefficients. The most probable value for E^0_{25} is −0.1519 v. This agrees fairly well with Owen's value, probably as well as could be expected.

Extrapolations at the other temperatures are less reliable than at 25° because only part of the cells were measured at any one temperature. Therefore, the electromotive forces were cor-

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(4) (a) Ref. 1; (b) Bates, THIS JOURNAL, **60**, 2984 (1938); (c) Vosburgh, Derr, Cooper and Bates, *ibid.*, **61**, 2592 (1939).

(5) Popoff, Kunz and Snow, *J. Phys. Chem.*, **32**, 1059 (1928).

(6) Clayton and Vosburgh, *ibid.*, **59**, 2414 (1937).

(7) Harned and Ehlers, *ibid.*, **55**, 652 (1933).

(8) Kielland, *ibid*, **59**, 1677 (1937).

rected by the addition of 0.07 mv. for Group 1 or 0.16 mv. for the other cells, these being the corrections made at 25°. The values of E^0 at the various temperatures are shown in Table II.

TABLE II

E^0_t FOR THE CELL H_2/HI (a = 1)/AgI, Ag

Group no.	No. of cells	E^0_{10}	E^0_{15}	E^0_{20}	E^0_{25}
1a	2	−0.14769	−0.14894	−0.15038	−0.15195
4a	2	− .14767	− .14890	− .15037	− .15191
Calcd., Eq. 2		− .1476	− .1489	− .1503	− .1519
		E^0_{25}	E^0_{30}	E^0_{35}	E^0_{40}
1b	2	−0.15182	−0.15350	−0.15553	−0.15731
3	1	− .15189	− .15350	− .15544	− .15720
4b	2	− .15192	− .15367	− .15551	− .15724
Calcd., Eq. 2		− .1519	− .1536	− .1555	− .1575

The equation

$$E^0_t = 0.1519 + 0.000328\,(t - 25) + 0.0000028\,(t - 25)^2 \qquad (2)$$

fits the data. The constant of the t term is the same as the corresponding constant in Owen's equation, while the second constant is a little smaller.

Summary

Measurements have been made at several temperatures of the electromotive force of the cell $H_2/HI/AgI$, Ag, with an acetate buffer containing potassium iodide as the electrolyte, and the values of E^0 calculated.

DURHAM, NORTH CAROLINA RECEIVED APRIL 8, 1940

[CONTRIBUTION FROM THE DEPARTMENT OF ANALYTICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

Color Phenomena Associated with Quinquevalent Molybdenum Solutions. I. Absorption Spectra in Solutions of Various Hydrochloric Acid Concentration

BY C. F. HISKEY* AND V. W. MELOCHE

Historical

The work reported herein was begun in connection with a series of studies designed to determine the best conditions under which rhenium and molybdenum could be separated from each other. In one group of experiments attempts were made to separate the quinquevalent molybdenum with butyl acetate by preferential extraction from concentrated hydrochloric acid solutions. During the preparation of this solution as well as in a previous study[1] pronounced color changes were observed in the quinquevalent molybdenum solution as the concentration of hydrochloric acid was altered. Such phenomena had been observed by Chilesotti,[2] who studied the electro-reduction of molybdates. Later a more detailed study of the molybdate reduction was made by Foerster and Fricke[3] and by Foerster, Fricke and Hausswald,[4] who showed that on addition of one equivalent of reductant a solution was formed whose color depended on the acid concentration. In 2 N hydrochloric the solution was amber, but in 8 N hydrochloric it was green.

From solutions of a high hydrochloric acid concentration they succeeded in isolating alkali salts of the general formula M_2MoOCl_5, leading them to believe that this green color was due to $MoOCl_3$ dissolved in the solution. Somewhat earlier Barbieri[5] also had observed that Klason's salt $(NH_4)_2MoOCl_5$, when treated with ammonium hydroxide, would precipitate an insoluble molybdenum penta-hydroxide which dissolved in dilute hydrochloric acid to form amber solutions. By concentrating this solution and saturating it with hydrogen chloride he was able to re-separate green crystals of Klason's salt. This would seem to indicate that the compound $MoOCl_3$ plays a basic role in all of the color phenomena involved in these studies.

From a study of Klason's salt Scagliarini[6] concluded that when one added successive portions of water to green quinquevalent molybdenum solutions the resulting color changes could be explained by ascribing to hydrolysis. Since the products formed were too soluble to be crystallized, he was not able to isolate any of the hydrolytic substances formed. From precipitations made with hexamethylenetetramine he obtained compounds in which he believed the acidic nucleus of $(NH_4)_2Mo(OH)_4Cl_3$ existed. Later James and Wardlaw[7] isolated salts of the type of R-$(MoOCl_4 \cdot H_2O)$, and R$(MoO_2Cl_2 \cdot H_2O)$. These investigations, however, do not give any clear indication of the nature of the color transition.

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[1] Hiskey and Meloche, THIS JOURNAL, **62**, 1565 (1940).

[2] Chilesotti, *Z. Elektrochem.*, **12**, 146, 173, 197 (1906).

[3] Foerster and Fricke, *Z. angew. Chem.*, **36**, 458 (1923).

[4] Foerster, Fricke and Hausswald, *Z. physik. Chem.*, **A146** 81, 171 (1930).

[5] Barbieri, *Atti. accad. Lincei*, **25**, I, 775 (1916).

[6] Scagliarini, *ibid.*, **6**, 676 (1905).

[7] James and Wardlaw, *J. Chem. Soc.*, 2145 (1927).