The author of this investigation feels that E_8 and E_{15} are close to the minimum values given above and bases his opinion on the following considerations. Granting that the values reported for $k_7/k_8{}^2$ are not very accurate, since they were mainly determined from intercepts, they nevertheless indicate that E_8 is small. In an investigation of methyl acetate,[1] an activation energy of about 4.5 kcal. was obtained for reaction 20.

$$CH_3O + CH_3COOCH_3 \longrightarrow CH_3OH + CH_2COOCH_3 \quad (20)$$

Although the RO–H bond has been reported[17] as 100 kcal. for CH_3O–H and as 99 kcal. for C_2H_5O–H, it seems logical that E_{15} should not exceed E_{20} to any great extent, if at all. This is even more so if we consider that a primary hydrogen is abstracted in reaction 20 while a secondary hydrogen is abstracted from ethyl propionate.

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[17] P. Gray, *Trans. Faraday Soc.*, **52**, 344 (1956).

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS EXPERIMENT STATION, REGION II, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low Temperature Heat Capacities and Entropies at 298.15°K. of Lead Sesquioxide and Red and Yellow Lead Monoxide

BY E. G. KING[1]

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The heat capacities of lead sesquioxide and the red and yellow forms of lead monoxide were measured over the temperature range 51–298°K. All three substances behaved in a regular manner. Entropies at 298.15°K. were obtained, as shown (cal./deg. mole): sesquioxide, 36.3 ± 0.7; red monoxide, 15.6 ± 0.2; and yellow monoxide, 16.1 ± 0.2.

This paper reports heat capacity measurements over the temperature range 51–298°K., together with entropy evaluations at 298.15°K., for lead sesquioxide, red lead monoxide (tetragonal) and yellow lead monoxide (rhombic). No previous similar data have been published for these compounds except the few results of Nernst and Schwers[2] for the yellow monoxide in the temperature range 21–93°K. Data for lead dioxide and minium (Pb_3O_4) have been reported by Millar.[3]

Materials.—Lead sesquioxide was prepared by the following procedure. A solution of reagent grade lead nitrate was treated with a slight excess of ammonium carbonate solution. The precipitated lead carbonate was washed free of ammonium salts and dried at 140°. It then was converted to sesquioxide by heating in air, 40 hr. at 290°, 64 hr. at 310° and 10 days at 320°. Analysis of the product gave 89.64% lead, as compared with the theoretical 89.62%. The X-ray diffraction pattern agreed with the ASTM catalog.

Red lead monoxide was prepared by heating electrolytic lead dioxide *in vacuo* at 430–480° for about 8 weeks. (The long heating period was required to eliminate yellow monoxide which is very slow to convert to red.) The product gave no test for higher oxides when treated with strong sodium hydroxide solution. It analyzed 92.69% lead (theory, 92.83%). The X-ray diffraction pattern indicated the presence of only a small amount of the yellow variety.

Yellow lead monoxide was made by heating lead carbonate (obtained by the method mentioned above). The first heating, 80 hr. at 560–580°, was insufficient to decompose the carbonate completely or to prevent the formation of some red monoxide. The substance finally was split into small portions, heated for 10 hr. at 725° and quenched to room temperature. No reconversion to the red form occurred during this treatment. Analysis of the product gave 92.84% lead (theory, 92.83%). The X-ray diffraction pattern agreed with the ASTM catalog.

TABLE I

HEAT CAPACITIES (CAL./DEG. MOLE)

T, °K.	C_p	T, °K.	C_p	T, °K.	C_p
		Pb_2O_3 (mol. wt., 462.42)			
53.36	8.891	114.88	15.90	216.45	22.80
58.06	9.524	124.78	16.81	226.13	23.25
62.66	10.12	136.53	17.82	235.97	23.64
67.03	10.70	145.90	18.58	245.91	24.04
71.50	11.24	155.87	19.33	256.50	24.44
75.95	11.77	166.02	20.02	266.45	24.81
81.00	12.38	175.85	20.62	276.38	25.09
85.48	12.87	186.19	21.25	287.09	25.40
94.96	13.91	196.05	21.78	296.56	25.70
104.75	14.92	206.42	22.33	298.15	(25.74)
		PbO (red, mol. wt., 223.21)			
53.40	4.095	114.78	7.039	216.27	9.878
58.07	4.354	124.89	7.440	226.09	10.05
62.71	4.608	135.91	7.841	236.73	10.21
67.26	4.851	145.79	8.183	245.91	10.32
71.67	5.088	155.84	8.494	256.39	10.47
76.13	5.311	165.83	8.773	266.62	10.60
81.30	5.559	176.34	9.039	276.58	10.71
85.97	5.777	186.35	9.283	286.79	10.82
94.64	6.179	195.99	9.479	296.27	10.94
104.71	6.627	206.38	9.702	298.15	(10.95)
		PbO (yellow, mol. wt., 223.21)			
54.13	4.353	114.74	7.184	216.48	9.915
58.39	4.590	124.80	7.568	226.22	10.08
62.59	4.806	135.95	7.958	236.04	10.24
66.82	5.041	145.71	8.292	245.94	10.37
71.12	5.260	155.95	8.599	256.39	10.50
75.57	5.472	165.87	8.868	266.26	10.61
81.03	5.734	176.28	9.118	276.22	10.72
85.21	5.924	185.83	9.337	286.42	10.82
94.91	6.363	196.21	9.547	296.11	10.94
105.01	6.793	206.23	9.747	298.15	(10.95)

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[1] Bureau of Mines, U. S. Department of the Interior, Berkeley, California.

[2] W. Nernst and F. Schwers, *Sitzber. preuss. Acad. Wiss.*, 355 (1914).

[3] R. W. Millar, THIS JOURNAL, **51**, 207 (1929).

Measurements and Results

The heat capacity calorimeter and method of operation have been described.[4] Results are reported in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole. All weighings were corrected to vacuum and molecular weights accord with the 1954–55 Report on Atomic Weights.[5] The masses of the compounds used in the measurements were 184.16 g. of sesquioxide, 407.98 g. of red monoxide and 487.04 g. of yellow monoxide.

The measured heat capacity values are listed in Table I. The heat capacity of the yellow monoxide exceeds that of the red by 5.7% at 50°K., decreasing to 2.6% at 100°K. and to zero at 298°K. Using the data of Millar[3] for the dioxide, it is observed that the heat capacity of the sesquioxide is less than the sum for the dioxide and either of the monoxides at temperatures above about 150°K.; at lower temperatures the reverse holds.

Entropies at 298.15°K.—The entropy increments between 51.00 and 298.15°K. were obtained by Simpson-rule integrations of C_p against log T plots. The extrapolated portions of the entropies (0–51.00°K.) were obtained from these empirical combinations of Debye and Einstein functions, which fit the measured heat capacities within the limits indicated:

Pb_2O_3: $D(79.4/T) + 2E(220/T) + 2E(653/T)$ (51–298° K.; 2.0%)
PbO(red): $D(156/T) + E(481/T)$ (51–250°K.; 1.3%)
PbO(yellow): $D(145/T) + E(473/T)$ (51–250°K.; 1.0%)

The results of the entropy calculations are in Table II.

TABLE II

ENTROPIES (CAL./DEG. MOLE)

Substance	S^0_{51} (extrap.)	$S^0_{298.51} - S^0_{51}$ (meas.)	$S^0_{298.15}$
Pb_2O_3	6.51	29.80	36.3 ± 0.7
PbO(red)	2.48	13.11	15.6 ± .2
PbO(yellow)	2.78	13.33	16.1 ± .2

The entropy of yellow lead monoxide is 0.5 cal./deg. mole less than the result estimated by Kelley[6] from the data of Nernst and Schwers.[2] According to Table II, the entropy of transformation of red to yellow monoxide is $\Delta S^0_{298.16} = 0.5$. This value may be projected to the equilibrium point (762°K.)[7] by means of the high temperature data listed by Kelley.[8] The result is $\Delta S^0_{762} = 0.2$, corresponding to a heat of transformation of 150 cal./mole. The latter is equivalent to $\Delta H_{298} = 270$ cal./mole, which agrees substantially with the difference in heats of formation (330 cal.) given in NBS Circ. 500.[9]

(4) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

(5) E. Wichers, THIS JOURNAL, **78**, 3235 (1956).

(6) K. K. Kelley, U. S. Bur. Mines Bull. 477 (1950).

(7) A. Silverman, H. Insley, G. W. Morey and F. D. Rossini, Natl. Research Council Bull. 118 (1949).

(8) K. K. Kelley, U. S. Bur. Mines Bull. 476 (1949).

(9) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, Natl. Bur. Standards Circ. 500 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Mechanisms of Exchange Reactions between Elementary Iodine and Aromatic Iodides

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The thermal exchange of elementary iodine with iodobenzene and with *p*-nitroiodobenzene has been studied in the solvents hexachlorobutadiene-1,3 and nitrobenzene. Two independent processes contribute to the rate. One process is the expected direct radical exchange between an iodine atom and a molecule of aromatic iodide. The rate constants for this process are not significantly affected by change of solvent, but substitution with a *p*-nitro group slows the rate somewhat. This effect of substitution is opposite to the direction usually predicted and observed for radical reactions. The other exchange process is second order in aromatic iodide and is usually *zero* order in iodine. Change of solvent from hexachlorobutadiene to nitrobenzene inhibits this process for iodobenzene but accelerates it for *p*-nitroiodobenzene. When both aromatic iodides are present in a solution, the rate constant for the exchange process involving one molecule of each is greater than the rate constant for either process involving two identical molecules. We propose that this exchange process involves reversible formation of a diphenyliodonium iodide ion pair and rapid exchange of molecular iodine with the iodide portion of it. The proposed mechanism explains some peculiar observations reported previously on the exchange of iodobenzenes with sodium iodide. These aromatic iodides also decompose with formation of molecular iodine. The rates are erratic but seem to follow first-order kinetics when only one aromatic iodide is present. If both iodobenzene and *p*-nitroiodobenzene are present, an additional decomposition is ascribed to rearrangement of the diphenyliodonium iodide ion pair to form iodine and a monosubstituted diphenyl.

Introduction

The results reported in this paper are part of a program of study of the mechanisms of exchange reactions in solution between isotopically labelled elementary iodine and various organic iodine compounds. The primary objective of the studies is to obtain quantitative information about the reactions of iodine atoms in the expectation that this information will be of value in the interpretation of other more complicated reactions involving free radicals. However, the present investigation and some others have demonstrated the existence of unexpected non-radical reactions taking place in certain systems.

Experimental

Materials.—Iodobenzene was prepared by the diazotization of freshly distilled aniline.[2] The resulting product was washed with hydrochloric acid and sodium carbonate

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(1) The data on which this paper is based are contained in the Ph.D. Dissertation of Samuel Levine. The original dissertation and microfilms thereof are available from the Library of Columbia University.

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(2) "Organic Syntheses," Vol. II, edited by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 351.