The yields by both processes A and B are affected adversely by the presence of water in the reagents.

TABLE I

GLYCOL ETHERS PREPARED

Glycol ether	Formula	Boiling point °C.	Boiling point Mm.	Yield by method A %	Yield by method B %	d_{15}^{15}	Analysis Calc. C %	Analysis Calc. H %	Analysis Found C %	Analysis Found H %
Mono-methyl[a]	.....	124.5	743	26	35	....	...	...	...	...
Mono-ethyl[b]	.....	134.8	743	50	60	....	...	...	...	...
Mono-*iso*propyl	$C_5H_{12}O_2$	144	743	31	25	0.9115	57.64	11.61	57.35	11.46
Mono-propyl[c]	$C_5H_{12}O_2$	150	743	50	40	.9141	57.64	11.61	57.85	11.94
Mono-*iso*butyl	$C_6H_{14}O_2$	158.8	743	42	36	.8950	60.96	11.94	60.41	11.75
Mono-butyl	$C_6H_{14}O_2$	170.6	743	40	30	.9011	60.96	11.94	61.03	12.02
Mono-amyl	$C_7H_{16}O_2$	181	745	42	30	.8926	63.58	12.20	63.43	12.38

[a] Ref. 3 b, p. 3874. Palomaa gives b. p., 124.9° (768 mm.).

[b] Palomaa gives b. p., 134.7–134.9° (748 mm.).

[c] Prepared by Palomaa but not analyzed.

Summary

1. A simple method for the preparation of alkyl ethers of ethylene glycol has been developed.
2. Several new compounds in this series have been prepared.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

THE SPECIFIC HEATS OF TRINITROTOLUENE, TETRYL, PICRIC ACID AND THEIR MOLECULAR COMPLEXES[1]

BY C. A. TAYLOR[2] AND WM. H. RINKENBACH[3]

RECEIVED MARCH 15, 1924

At the suggestion of Dr. C. E. Munroe of the National Research Council, the Explosives Chemical Laboratory of the Bureau of Mines has undertaken the determination of some of the hitherto undetermined constants of explosive compounds.

The only data on the specific heats of the substances covered by this paper are those by Prentiss[4] on the mean specific heats of trinitrotoluene and tetryl as determined by the method of mixtures.

Method of Determination

The liquid oxygen calorimeter first described by Dewar[5] was used. The apparatus consisted of a small Dewar flask of about 50cc. capacity,

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[1] Published by permission of the Director, U. S. Bureau of Mines.

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[4] Prentiss, "Specific Heats and Thermal Diffusivities of Certain Explosives," *Army Ordnance*, vol. **4**, 1923, pp. 117, 184, 242.

[5] Dewar, *Chem. News*, **92**, 181 (1905).

of greater length than diameter, and having a narrow neck about 25 cm. in length, with a side tube attached to its upper part. A short piece of heavy-walled rubber tubing connects the neck of the flask with a small, thin-walled test-tube.

This small flask was half-filled with liquid oxygen and immersed in a Dewar flask of 2 to 4 liters' capacity; this outer flask was filled with liquid oxygen and carefully insulated with felt or cotton batting to minimize heat absorption, while the space between the neck of the two flasks was packed with felt. A tube was connected to the side-arm of the small Dewar flask so that the evolved gas could be collected over water or mercury in a graduated tube, preferably one of 100cc. capacity and graduated to 0.2 cc.

A weighed portion of the substance to be investigated was placed in the small test-tube, which was connected with the neck of the small Dewar flask by rubber tubing. The test-tube was immersed in a bath of known temperature, and the contents allowed to attain that temperature. The system was then closed, and when temperature equilibrium was established, no gas was evolved. By elevating the test-tube, the substance being tested was quickly dropped into the liquid oxygen contained in the small flask. The heat energy released by the fall in temperature of the substance from that of the bath to that of liquid oxygen vaporized some of the liquid oxygen, which was collected in the measuring tube. This tube was lowered in a bath until the vaporized oxygen was under atmospheric pressure, and the volume of gas collected was recorded without correction to standard conditions of temperature and pressure.

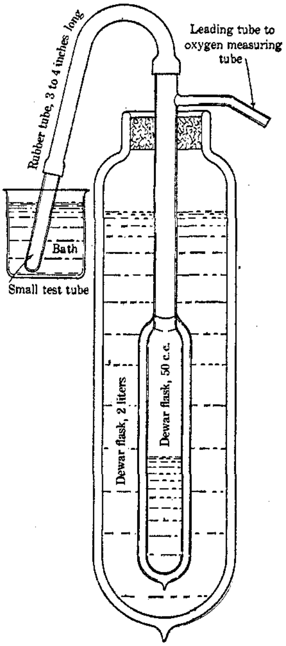

Fig. 1.—Specific-heat apparatus.

Determinations were made alternately on the material under test and on pure lead, the specific heat of which is known, so that all measurements were strictly comparative. It was thus possible to eliminate calculation

Table I

Specific Heat of Lead

°C.	Sp. ht.	°C.	Sp. ht.	°C.	Sp. ht.
−128.8	0.02757	−75	0.02914	50	0.03089
−175	.02768	−50	.02949	75	.03123
−150	.02805	−25	.02984	100	.03155
−125	.02943	0	.03020	125	.03192
−100	.02880	25	.03054	...	....

to standard conditions of the oxygen evolved, and the effects of small differences in different "batches" of liquid oxygen were eliminated.

The specific heat of lead has been accurately determined, and is practically a linear function of the temperature. By plotting the data and deriving a curve, the values in Table I were obtained by interpolation.

It was possible to calculate the specific heat of lead (mean) over any desired range by averaging the values for the two extremes of the range.

The method was checked by determining the specific heat of naphthalene and comparing the results obtained with those of Battelli.[6] The data obtained by the liquid-oxygen calorimeter and the calculated specific heats follow.

TABLE II

MEAN SPECIFIC HEAT OF NAPHTHALENE COMPARED WITH THAT OF LEAD

Temperature °C.	Material	Weight		Oxygen evolved, cc. per gram sample		Mean sp. ht. over this range
−182.8 to 0	Lead	0.8553	0.8470	91.4	88.6	0.02889
		0.8227		89.7		...
	Naphthalene	.1495	.1263	555.2	546.3	...
		0.1240		556.3		.178
−182.8 to 24	Lead	.7160	.7135	96.9	98.7	...
		.7197	.7178	101.4	98.3	.02905
	Naphthalene	.1050	.1055	651.4	655.9	.192
−182.8 to 79	Lead	.6607	.6463	119.0	114.1	.02943
		0.6545		110.6		...
	Naphthalene	.0758	.0708	862.8	830.5	.220

The results for naphthalene plotted against the corresponding maxima of the temperature ranges gave a curve of semi-cubic parabola type, $y = A + Bx - Cx^2$, the curvature being so slight that powers beyond the second could be disregarded. The equation of this curve was found to be $y = 0.178 + 0.000665728x - 0.000001697x^2$, where y represents the mean specific heat from —182.8° to x°.

From this equation the mean specific heat of naphthalene over any desired range was calculated by multiplying each value of the specific heat from —182.8° to each terminus of the range by the corresponding number of degrees in the range, subtracting the smaller from the greater value, and dividing the difference by the number of degrees in the temperature range under calculation. The following values were derived as compared with those found by Battelli.

Temp. range, °C.	10–20	40–50	60–70
Sp. heat, found	0.309	0.321	0.324
Sp. heat, Battelli	.314	.326	.334

Dewar's experimental data for the specific heat of naphthalene are as follows.

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[6] Battelli, *Atti ist. Veneto* [6] **3,** disp. 10, 1781 (1884–1885).

Temperature, °C........	−188 to +15	−188 to +16	−188 to +16
Sp. heat................	0.204	0.202	0.194

Mean Specific Heat of Trinitrotoluene

Material.—The trinitrotoluene was from the same lot used in determining the temperature-concentration curves[7] of the system TNT-tetryl and TNT-picric acid. It was pure white, finely divided, and had a setting point of 80.27°. It was placed in a test-tube, melted, and allowed to cool to room temperature. The tube was then broken away from the melt, and the solid was broken up into small lumps. The following results were obtained.

TABLE III

MEAN SPECIFIC HEAT OF TRINITROTOLUENE COMPARED WITH THAT OF LEAD

Temperature range °C.	Material	Weight		Cc. of oxygen per gram		Mean sp. ht.
−182.8 to 0	Lead	0.8347	0.8205	76.0	74.1	0.02889
		.8310	.8373	72.8	73.8	...
	TNT	.1447	.1487	483.7	478.8	.188
		.1420	.1535	483.1	487.3	...
−182.8 to 20.2	Lead	.7273	.7390	86.9	89.4	.02904
		.7212	.7250	92.5	90.2	...
	TNT	.1247	.1220	628.7	608.2	.201
−182.8 to 79	Lead	.6607	.6647	108.0	104.1	.02943
		.6668	.6583	107.7	104.2	...
	TNT	.0710	.0797	845.0	846.9	.235
		0.0738		844.1		...

The average mean specific heats of trinitrotoluene over these ranges were plotted, and found to form a semi-cubic parabola of very slight curvature, the equation of which was $y = 0.188 + 0.00066027x - 0.000000827x^2$.

TABLE IV

MEAN SPECIFIC HEAT OF TETRYL COMPARED WITH THAT OF LEAD

Temperature range °C.	Material	Weight		Cc. of oxygen per gram		Mean sp. ht.
−182.8 to 0	Lead	0.8200	0.8490	76.6	72.1	0.02889
		.8388	.8240	73.3	77.1	...
	Tetryl	.1570	.1600	490.5	485.5	.188
		0.1590		487.4		...
−182.8 to 22.5	Lead	.8480	.8185	82.0	80.6	.02904
	Tetryl	.1070	.1490	532.7	533.6	...
		.1532	.1070	540.5	532.7	.191
−182.8 to 97	Lead	.7615	.7528	125.7	125.1	...
		0.6165		122.1		.02931
	Tetryl	.0713	.0690	841.5	847.8	...
		0.0590		856.0		.200

These results gave a curve of equation, $y = 0.000136239x - 0.00000012915x^2 + 0.188$.

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[7] Taylor and Rinkenbach, *J. Ind. Eng. Chem.*, **15**, 73, 795 (1923).

TABLE V

MEAN SPECIFIC HEAT OF PICRIC ACID

Temperature range °C.	Material	Weight		Cc. of oxygen per gram		Mean sp. ht.
−182.8 to 0	Lead	0.8090	0.8532	78.6	81.1	...
		.8130	.8750	76.7	78.8	0.02889
	Picric acid	.1413	.1485	482.6	474.1	.176
		.1477	...	478.5	...	...
−182.8 to 19	Lead	.8575	.8468	87.9	87.9	.02901
	Picric acid	.1405	.1470	552.3	548.3	.182
		.1462	...	550.6	...	...
−182.8 to 98.1	Lead	.6215	.6018	106.3	109.3	...
		.6328	.6312	105.1	107.4	.02956
	Picric acid	.0682	.0915	766.8	761.7	...
		.0860	.0967	753.5	761.4	.210
−182.8 to 121.5	Lead	.5525	.5500	123.8	127.8	.02972
	Picric acid	.0813	.0808	913.9	933.2	...
		.0755	.0717	910.0	945.6	.219

These values gave a curve of equation, $y = 0.176 + 0.00318985x + 0.00000029886x^2$.

Mean Specific Heat of the Molecular Compound Tetryl-2-trinitrotoluene

This compound was synthesized by melting together suitable weights of the component compounds and allowing the resultant liquid to crystallize. The mass was broken up into small pieces. The results obtained follow.

TABLE VI

MEAN SPECIFIC HEAT OF TETRYL-2 TNT COMPLEX

Temperature range °C.	Material	Weight		Cc. oxygen per gram		Mean sp. ht.
−182.8 to 0	Lead	0.8372	0.8278	80.3	81.1	...
		.8353	.8492	76.2	...	.02889
	Compound	.1350	.1380	503.7	505.1	.182
		.1367	...	501.8	...	...
−182.8 to 21	Lead	.7785	.8022	83.2	83.0	...
		.7707	.7753	82.0	85.4	.02903
	Compound	.1212	.1220	544.5	555.7	...
		.1253	.1285	561.9	560.3	.194
−182.8 to 45	Lead	.6308	.6505	96.4	95.5	...
		.6135	.6485	93.9	99.2	.02916
	Compound	.1017	.1045	687.3	684.2	.207
−182.8 to 60	Lead	.5535	...	105.15	...	.02929
	Compound	.0967	.1030	772.0	769.2	.215

When plotted in the usual way, a curve is formed of equation, $y = 0.181 + 0.000579489x - 0.0000002137x^2$.

Mean Specific Heat of the Molecular Compound Tetryl Picric Acid

This compound was synthesized in a manner similar to that used for the compound of tetryl and trinitrotoluene. The following results were obtained:

TABLE VII

MEAN SPECIFIC HEAT OF TETRYL-PICRIC ACID COMPOUND

Temperature range °C.	Material	Weight		Cc. of oxygen per g.		Mean sp. ht.
−182.8 to 0	Lead	0.8138	0.8230	77.0	74.5	...
		.8067	.8237	75.0	77.2	0.02889
	Compound	.1423	.1458	501.7	497.3	...
		.1458	...	495.9	...	.190
−182.8 to 19.5	Lead	.7540	.7503	89.1	87.2	.02902
	Compound	.1035	.1058	591.3	596.2	...
		.1040	...	601.9	...	.196
−182.8 to 21.5	Lead	.7413	.7485	78.0	79.9	.02903
	Compound	.1200	.1195	532.8	544.0	.198
−182.8 to 79.5	Lead	.6550	.6510	118.8	118.7	.02943
	Compound	.0520	.0742	880.8	884.1	...
		.717	...	881.4	...	.218

These results gave a straight-line curve, the equation of which was found to be, $y = 0.190 + 0.0003522x$.

Specific Heats

The specific heats were calculated at 10° intervals from zero to the melting point of the material, by the use of the equation developed for the mean specific heat. The specific heat of trinitrotoluene at 50° was determined as follows. The mean specific heats from —182.8° to 49°, 50° and 51° were calculated from the equation and found to be 0.21837, 0.21895, and 0.21952, respectively. Multiplying each by the value °C. + 182.8 and subtracting the first from the second and the second from the third, gave the specific heats from 49° to 50°, and 50° to 51°. The average of these two values gives the specific heat of trinitrotoluene at 50°. Values at other temperatures were determined in the same way, and these values are listed in Table VIII.

TABLE VIII

SPECIFIC HEATS

Temperature °C.	Tetryl	Picric acid	TNT	Tetryl: picric acid	Tetryl: 2 TNT
0	0.213	0.234	0.309	0.254	0.287
10	.215	.242	.319	.261	.298
20	.217	.250	.328	.268	.308
30	.219	.258	.337	.276	.319
40	.221	.266	.345	.283	.329
50	.223	.274	.353	.290	.339
60	.225	.282	.361	.297	.349
70	.226	.291	.368	.304	..
80	.228	.300	.374	.311	..
90	.229	.309	..	..	..
100	.231	.318	..	..	..
110	.233	.327	..	..	..
120	.234	.337	..	..	..
125	.235	..	..	..	..

Summary

1. The specific heats of tetryl, picric acid, trinitrotoluene, tetryl:-picric acid, tetryl: 2 trinitrotoluene, have been measured over a range of temperature from 0° to 60° to 125°.

2. The values obtained indicate that Kopp's law does not hold for trinitrotoluene, tetryl or picric acid.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE COLLEGE OF LIBERAL ARTS OF NORTHWESTERN UNIVERSITY, AND THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE DIRECT MERCURATION OF BENZENE AND THE PREPARATION OF MERCURY DIPHENYL[1]

BY J. LEWIS MAYNARD

RECEIVED MARCH 17, 1924

There are to be found in the literature ten reactions involving the formation of mercury diphenyl.[2] However, the preparation of a considerable quantity of the mercury diaryl by any one of these methods is unsatisfactory because of the low yield obtained. Phenylmagnesium bromide and mercuric chloride give a 44% yield,[3] while the action of 2.7% sodium amalgam on bromobenzene results in a 46% yield.[4] In the other eight reactions either the yields are not given, or the mercury diphenyl appears only in small amounts as a by-product. During the past year the author has had occasion to prepare considerable quantities of mercury diphenyl, and it was deemed advisable to develop a more satisfactory method of preparation.

An important general reaction of organic mercury compounds involves the transformation of R-HgX to R_2Hg. Very few complications were met, so this process was selected for development. Of the many inorganic reagents capable of bringing about this change,[5] alkaline sodium stannite solution gave the best result: $2C_6H_5\text{-}HgX + Na_2SnO_2 + 2NaOH \longrightarrow (C_6H_5)_2Hg + Hg + 2NaX + Na_2SnO_3$. Mercury diphenyl and mercury are the only water-insoluble products formed, and they can easily be separated from each other. The reaction has been mentioned in an article on mercuration,[6] but quantitative data are lacking.

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[1] Presented at the Milwaukee meeting of the American Chemical Society, September, 1923.

[2] For a bibliography see Frank C. Whitmore, "Organic Compounds of Mercury," (American Chemical Society Monograph Series), Chemical Catalog Co., **1921**, pp. 163–164.

[3] Pfeiffer and Truskier, *Ber.*, **37**, 1127 (1904).

[4] Aronheim, *Ann.*, **194**, 148 (1878).

[5] Ref. 2, p. 40.

[6] Dimroth, *Ber.*, **35**, 2853 (1902).