tents which was established within 0.003° by means of a platinum resistance thermometer. The liquid sample within the calorimeter was agitated by a small centrifugal impeller. The energy measurements were made in watt-seconds and were converted to mean gram calories by the relation

1 thermochemical calorie = 4.1840 abs. joules

The apparatus was calibrated by measurements with water for which accurate thermodynamic data are available. The volume of the gas phase was maintained at less than 2.5% of the total volume of the calorimeter, and therefore simplifying assumptions in the calculations of the heat capacity from the thermal data are justified at temperatures below 100°.[5]

The hydrazine–water mixtures were prepared by diluting nearly pure hydrazine with distilled water and by refluxing the mixture at low pressures to remove dissolved gases. The compositions of the mixtures were determined from the quantity and composition of the hydrazine used and the weight of water added. It was found as a result of careful chemical analyses that the hydrazine contained less than 0.001 mole fraction of impurities. Analyses of the mixtures were also made and good agreement with the compositions computed from the gravimetric data was realized. Limited decomposition of the mixtures rich in hydrazine was evidenced at higher temperatures during the heat capacity measurements.

Results

Smoothed values of the isobaric heat capacity of the hydrazine–water system at bubble point are shown in Table I for compositions from 0.5 to 1.0 weight fraction hydrazine in the temperature range from 40 to 90°. The maximum error of the heat capacity data is estimated to be 1%, and 75% of the values recorded in Table I probably do not involve uncertainties greater than 0.5%. In Fig. 1 is presented the heat capacity of pure hydrazine as a function of temperature and, for comparison, data reported in the literature[6] for this compound are also included. The smoothed heat capacity data for the hydrazine–water system are depicted in Fig. 2. Density measurements were made with a pycnometer for a number of mixtures at compositions between 0.5 and 1.0 weight fraction hydrazine at temperatures between 0 and 50°. The smoothed data are presented in Table II and it is unlikely that they involve uncertainties larger than 0.1%.

TABLE I

SMOOTHED VALUES OF ISOBARIC HEAT CAPACITIES OF HYDRAZINE–WATER SYSTEM AT BUBBLE POINT

Composition wt. fract. hydrazine	Isobaric heat capacity, cal./g., °C. 40°	50°	60°	70°	80°	90°
0.50	0.8511[a]	0.8605[a]	0.8761	0.8943	0.9126	0.9306[a]
.60	.8351[a]	.8430[a]	.8546	.8673	.8783	.8887[a]
.70	.8152[a]	.8230[a]	.8313	.8404	.8483	.8554[a]
.80	.7902	.7985	.8057	.8134	.8203	.8258[a]
.90	.7632	.7721	.7796	.7864	.7927	.7987[a]
1.00	.7368	.7443	.7517	.7593	.7665	.7742[a]

[a] These values are extrapolated.

TABLE II

DENSITIES OF HYDRAZINE–WATER MIXTURES

Composition, wt. fract. hydrazine	Density 0°	50°
0.50	1.0078	1.0050
.60	1.0074	1.0046
.70	1.0063	1.0030
.80	1.0014	0.9976
.90	0.9925	.9893
1.00	.9816	.9780

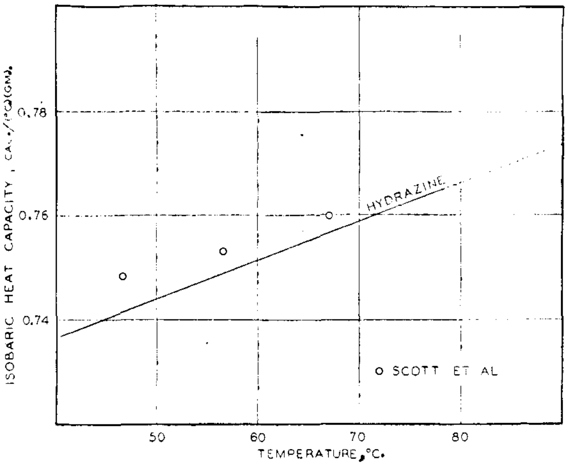

Fig. 1.—Isobaric heat capacity of hydrazine at bubble-point pressure.

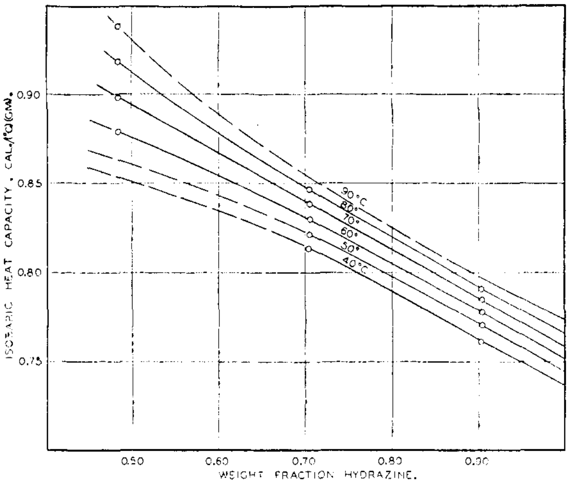

Fig. 2.—Isobaric heat capacity of the hydrazine–water system.

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(6) D. W. Scott, *et al.*, THIS JOURNAL, **71**, 2293 (1949).

Heat Capacities of Several Organic Liquids[1]

BY E. W. HOUGH,[2] D. M. MASON AND B. H. SAGE

The isobaric heat capacities of aniline, ethylenediamine, furfuryl alcohol, isopropylamine, methyl

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(1) This paper presents the results of one phase of research carried out for the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. W-04-200-ORD-1482 sponsored by the U. S. Army Ordnance Department.

(2) Stanolind Oil and Gas Company, Tulsa, Oklahoma.

alcohol and nitromethane were determined in a stainless steel bomb calorimeter at bubble point. The measurements were made at temperatures from 20 to 100°, except for aniline for which the maximum was 180°.

Experimental

The calorimeter used in establishing the heat capacities of these liquids and the technique of measurements have been described in detail elsewhere.[3,4,5] Essentially, the equipment consisted of a vacuum jacket within which a stainless steel bomb-type calorimeter of approximately 1-liter volume was suspended by small wires. An electrical heater was used to raise the temperature of the calorimeter and contents. The change in temperature was measured with an uncertainty of 0.003° by means of a platinum resistance thermometer. The contents of the calorimeter were agitated by a small centrifugal impeller. Integrated values of the energy added to the calorimeter involved a probable error of not more than 0.05%. The over-all accuracy of the apparatus was checked by measurements with water for which accurate thermodynamic data are available.

Results

The samples of organic liquid listed in Table I were obtained from commercial sources and were subjected to distillation at reduced pressure to insure the removal of dissolved gases. The materials as purchased were reputed to contain less than 0.002 mole fraction of impurities and in each case the indicated impurity possessed a heat capacity very similar to that of the compound in question.

The purity of each compound was checked by comparing its index of refraction relative to the D-lines of sodium with values given in the literature. The agreement of the measured values with those reported in the literature indicates that the samples probably contained less than 0.002 mole fraction of the principal impurity reported by the vendor. These comparisons are shown in Table I. The densities of the samples of the liquids at several temperatures at atmospheric pressure are recorded in Table II.

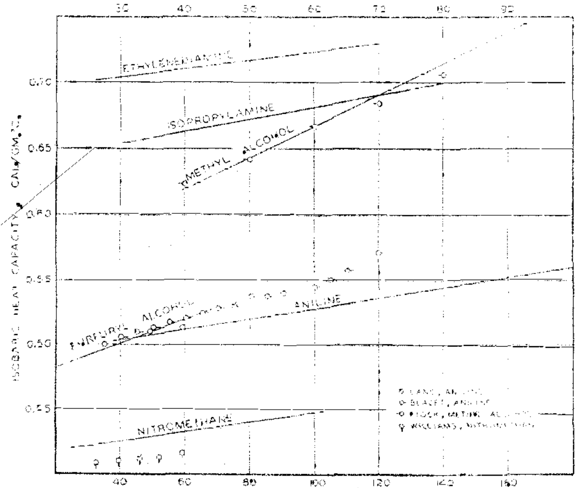

Fig. 1.—Isobaric heat capacity of several organic liquids.

TABLE I

REFRACTIVE INDICES OF SAMPLES AT 25°

Liquid	Index of refraction[a] Measured	Index of refraction[a] Literature
Aniline	1.5826	1.5863[b,c]
Ethylenediamine	1.4553	1.4552[d]
Furfuryl alcohol	1.4831	1.4850[e]
Isopropylamine	1.3724	1.3720[f,d]
Methyl alcohol	1.3270	1.3271[g]
Methyl alcohol	....	1.3267[h,f]
Nitromethane	1.3800	1.3818[e,b]

[a] Index of refraction relative to the D-line of sodium. [b] Value at 20°. [c] "International Critical Tables," 7, 38, McGraw-Hill Book Co., Inc., New York, N. Y., 1930. [d] J. W. Brühl, *Z. physik. Chem.*, **16**, 214 (1895). [e] "Handbook of Chemistry and Physics," 31st Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1949, p. 851. [f] These values are extrapolated. [g] J. W. Brühl and H. Schröder, *Z. physik. Chem.*, **50**, 10 (1905). [h] J. Timmermans and Mme. Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1930).

TABLE II

SMOOTHED VALUES OF DENSITY OF ORGANIC LIQUIDS

Temp., °C.	Aniline	Ethylenediamine	Furfuryl alcohol	Isopropylamine	Methyl alcohol	Nitromethane
20				0.6904[a]		
30		0.8985	1.124	.6798		1.112[b]
40	1.0057[a]	.8897	1.114	.6694		
50	0.9966	.8809	1.105	.6589	0.7632	
60	.9874	.8720	1.095	.6485	.7536	
70	.9785	.8631	1.086[a]	.6380	.7442	
80	.9692	.8543		.6276[a]	.7347	
90	.9602				.7251	
100	.9510					
120	.9329					
140	.9147					
160	.8964					
180	.8781					

[a] These values are extrapolated. [b] Value at 32.22°C.

The thermal data yielding directly the heat capacity in the two-phase region were modified by appropriate thermodynamic corrections[3,5] to obtain values of the isobaric heat capacity at bubble point. Smoothed values of the isobaric heat capacities are presented in Fig. 1 and Table III. It is estimated that these data involve a probable error of approximately 0.4%. In Fig. 1 also are shown values of the heat capacities available from the literature.[6,7,8,9,10,11] The energy measurements were made in watt-seconds and were converted to thermochemical gram calories by the relation

$$1 \text{ thermochemical calorie} = 4.1840 \text{ abs. joules}$$

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(3) B. H. Sage and E. W. Hough, *Anal Chem.*, **22**, 1304 (1950).

(4) W. P. White, "The Modern Calorimeter," (The Chemical Catalog Co.) Reinhold Publishing Corp., New York, N. Y., 1928.

(5) N. S. Osborne, H. F. Stimson and E. F. Fiock, *Natl. Bur. Standards J. Research*, **5**, 411 (1930).

(6) F. E. Blacet, P. A. Leighton and E. P. Bartlett, *J. Phys. Chem.*, **35**, 1935 (1931).

(7) A. Ferguson and J. T. Miller, *Proc. Phys. Soc. (London)*, **45**, 194 (1933).

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(9) G. S. Parks, H. M. Huffman and M. Barmore, THIS JOURNAL, **55**, 2733 (1933).

(10) E. F. Fiock, D. C. Ginnings and W. B. Holton, *Bur. Standards J. Research*, **6**, 881 (1931).

(11) J. W. Williams, THIS JOURNAL, **47**, 2644 (1925).

TABLE III

SMOOTHED VALUES OF ISOBARIC HEAT CAPACITIES OF ORGANIC LIQUIDS AT BUBBLE POINT

Temp. °C.	Aniline	Ethylenediamine	Furfuryl alcohol	Isopropylamine	Methyl alcohol	Nitromethane
20			0.482[a]			
30		0.704[a]	.491	0.653[a]		0.422[a]
40	0.503[a]	.710	.501	.663	0.620[a]	.426
50	.507	.716	.510	.673	.643	.429
60	.511	.723	.519	.683	.667	.432
70	.515	.730[a]	.529[a]	.693	.692	.436
80	.520			.703[a]	.715	.440
90	.524				.739[a]	.444
100	.528					.448[a]
120	.536					
140	.544					
160	.552					
180	.561					

[a] These values are extrapolated.

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Some *p*-Nitrophenyl Derivatives of *o*-Phosphoric and *o*-thiophosphoric Acid

BY J. A. A. KETELAAR AND H. R. GERSMANN

Several new compounds related to parathion (O,O′-diethyl O″-*p*-nitrophenyl thiophosphate) have been prepared.

O-Ethyl O′,O″- Bis-(*p*-nitrophenyl) Thiophosphate (I).—To 0.25 mole of thiophosphoryl chloride in 150 ml. of acetone was added in portions 0.5 mole of freshly dried powdered sodium *p*-nitrophenoxide, while stirring and cooling. The reaction proceeds rapidly even at 0°. After completion, 0.25 mole of sodium ethoxide in ethanol was added with cooling, and the mixture was poured into a large quantity of water. The precipitate was collected, washed, boiled with 500 ml. of ethanol and filtered hot. From the filtrate on cooling compound I separated and was recrystallized from ethanol, yield 25 g., m. p. 125–126°, colorless needles, soluble in acetone. *Anal.* Calcd. for $C_{14}H_{13}N_2O_7PS$: C, 43.73; H, 3.39; N, 7.29; S, 8.34; P, 8.06. Found: C, 44.36; H, 3.53; N, 7.04; S, 8.66; P, 8.26.[1]

O,O′,O″-Tris-(*p*-nitrophenyl) Thiophosphate (II).—The theoretical amount of sodium *p*-nitrophenoxide was added to thiophosphoryl chloride as described under I. The product is insoluble in boiling ethanol and can be obtained pure by recrystallization from acetone, yield 83%; very light yellow crystals, m. p. 174°. *Anal.* Calcd. for $C_{18}H_{12}N_3O_9PS$: C, 45.28; H, 2.52; N, 8.80; S, 6.71; P, 6.50. Found: C, 45.36; H, 2.44; N, 8.94; S, 6.88; P, 6.63.

The ethanol-insoluble portion of the preceding preparation is also tris-(*p*-nitrophenyl) thiophosphate. About 35 g. was obtained in this way, giving a total yield of I and II, based on sodium *p*-nitrophenoxide, of about 75%.

O-Methyl O′,O″-bis-(*p*-nitrophenyl) thiophosphate (III) was prepared using the same procedure as described for the ethyl homolog, but using sodium methoxide in methanol instead of sodium ethoxide. It melts at 96° and its properties are analogous to those of I; yield about 25% with 50% of compound II as a by-product. *Anal.* Calcd. for $C_{13}H_{11}N_2O_7PS$: C, 42.16; H, 2.98; N, 7.57; P, 8.38. Found: C, 42.28; H, 2.99; N, 7.71; P, 8.30.

Methyl Bis-(*p*-nitrophenyl) Phosphate (IV).—To 0.25 mole of phosphorus oxychloride and 100 ml. of dioxane was added 0.5 mole of sodium *p*-nitrophenoxide in portions while stirring and cooling. The temperature should be kept below 35°. After completion of this reaction 0.25 mole of sodium methoxide in methanol was added slowly. The mixture was stirred for about 30 minutes, poured into a large quantity of water and the residue collected. About 20 g. of IV, m. p. 141–142.5°, was obtained from this residue by treatment with boiling ethanol (see I). *Anal.* Calcd. for $C_{13}H_{11}N_2O_8P$: C, 44.07; H, 3.11; N, 7.91. Found: C, 43.96; H, 2.93; N, 7.87.

Ethyl bis-(*p*-nitrophenyl) phosphate (V) was prepared as described under IV, but using sodium ethoxide in ethanol instead of sodium methoxide. An analogous yield was obtained, m. p. 132–136°. *Anal.* Calcd. for $C_{14}H_{13}N_2O_8P$: C, 45.65; H, 3.54; N, 7.61; P, 8.41. Found: C, 45.51; H, 3.52; N, 7.68; P, 8.33.

Tris-(*p*-nitrophenyl) phosphate (VI) was prepared by adding 0.167 mole of phosphorus oxychloride in 100 ml. dioxane slowly to 0.5 mole of powdered dry sodium *p*-nitrophenoxide in 200 ml. of dioxane while stirring and cooling with ice-water. After addition the mixture was heated to 100°, filtered hot, and the precipitated sodium chloride washed with hot dioxane. From the combined filtrate compound VI separated on cooling; yield 50–60%, m. p. 156°, soluble in acetone. *Anal.* Calcd. for $C_{18}H_{12}N_3O_{10}P$: C, 46.85; H, 2.60; N, 9.10. Found: C, 46.66; H, 2.45; N, 9.22.

The portion of the residue insoluble in boiling ethanol in the preparation of compound IV or V is also tris-(*p*-nitrophenyl) phosphate. The total yield of bis- and tris-compound on the quantity of sodium nitrophenoxide used is about 50%.

We have also prepared by Schrader's method[2] the dimethyl analog of parathion, O,O′-dimethyl O″-*p*-nitrophenyl thiophosphate. It separates as white needles, m. p. 36.5°, from alcoholic solution. *Anal.* Calcd. for $C_8H_{10}NO_5PS$: C, 36.50; H, 3.81; S, 12.18; P, 11.80. Found: C, 36.54; H, 3.86; S, 12.07; P, 11.90.

Reduction of compound I and coupling with N-naphthylethylenediamine according to the method of Averell and Norris[3] for the determination of parathion also gives the same magenta color. However the presence of I in parathion can be detected by measuring the rate of hydrolysis.[4]

These compounds (I to VI) do not have significant activity as contact-insecticides (test insect, *calandra granaria*).

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[1] Micro-analyses were carried out by Messrs. P. J. Hubers and H. Pieters.

[2] G. A. Schrader, B I O S Final Report 1808, Synthetic Insecticides.

[3] P. R. Averell and M. V. Norris, *Anal. Chem.*, **20**, 753 (1948).

[4] J. A. A. Ketelaar, *Rec. trav. chim.*, **69**, 649 (1950).

Further Applications of the Schmidt Reaction

BY LESTER P. KUHN AND JEWELL DIDOMENICO

The reaction of olefinic compounds with hydrazoic acid probably involves a carbonium ion intermediate analogous to the oxocarbonium ion and the oxycarbonium ion postulated in the reaction of acids or carbonyl compounds with hydrazoic acid.[1] Although the Schmidt reaction has been widely used on acids and carbonyl compounds, it has been infrequently applied to olefins.[2] The reaction has now been applied to various substituted

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[1] (a) Newman and Gildenhorn, THIS JOURNAL, **70**, 317 (1948); (b) P. A. S. Smith, *ibid.*, **70**, 318 (1948).

[2] (a) German Patent 583,565 (*Frdl.*, **20**, 947 (1935); (b) C. Schuerch and E. H. Huntress, THIS JOURNAL, **71**, 2233, 2238 (1949); (c) W. E. McEwen, M. Gilliland and B. I. Sparr, *ibid.*, **72**, 3212 (1950).