TABLE I

ESTERS OF 3,4,5-TRIIODOBENZOIC ACID

Alcohol used	M. p., °C.	Yield, %	Formula	Iodine, % Calcd.	Iodine, % Found
Methyl	168.2–168.8[a]	36	$C_8H_5O_2I_3$	74.11	73.50
Ethyl	160.8–161.6	59	$C_9H_7O_2I_3$	72.12	72.40
n-Propyl	124.8–125.2[a]	63	$C_{10}H_9O_2I_3$	70.26	70.17
Isopropyl	133.7–134.2[a]	59	$C_{10}H_9O_2I_3$	70.26	70.71
n-Butyl	103.0–103.7	42	$C_{11}H_{11}O_2I_3$	68.48	68.84
Isobutyl	107.6–108.1	56	$C_{11}H_{11}O_2I_3$	68.48	69.05
s-Butyl	95.4–95.8	37	$C_{11}H_{11}O_2I_3$	68.48	68.18
n-Amyl	88.0–88.6	50	$C_{12}H_{13}O_2I_3$	66.80	66.73
Isoamyl	72.3–72.9	14	$C_{12}H_{13}O_2I_3$	66.80	65.93
2-Methyl-1-butanol	63.0–63.4	36	$C_{12}H_{13}O_2I_3$	66.80	67.11
2-Pentanol	72.6–73.4[a]	23	$C_{12}H_{13}O_2I_3$	66.80	67.11
3-Pentanol	74.4–75.6	27	$C_{12}H_{13}O_2I_3$	66.80	67.22
n-Hexyl	98.6–99.0	61	$C_{13}H_{15}O_2I_3$	65.21	65.42
2-Hexanol	99.1–99.9[b]	50	$C_{13}H_{15}O_2I_3$	65.21	65.21
n-Heptyl	58.5–58.9	30	$C_{14}H_{17}O_2I_3$	63.67	64.28
2-Heptanol	55.0–55.6[b]	23	$C_{14}H_{17}O_2I_3$	63.67	63.19
n-Octyl	71.2–71.8	51	$C_{15}H_{19}O_2I_3$	62.20	61.60
n-Nonyl	71.5–72.3	37	$C_{16}H_{21}O_2I_3$	60.81	61.11
n-Decyl	72.5–73.2[b]	50	$C_{17}H_{23}O_2I_3$	60.83	60.69
n-Dodecyl	76.9–77.3[b]	49	$C_{19}H_{27}O_2I_3$	56.99	57.07
Myristyl	80.2–81.2[a,b]	71	$C_{21}H_{31}O_2I_3$	54.69	54.58
Cetyl	79.9–80.8[a,b]	67	$C_{23}H_{35}O_2I_3$	52.57	52.58
Octadecyl	84.5–85.5[a,b]	74	$C_{25}H_{39}O_2I_3$	51.29	51.30
Cyclohexanol	151.1–151.9[a]	36	$C_{13}H_{13}O_2I_3$	65.42	65.29
Allyl	126.0–126.5[b]	58	$C_{10}H_7O_2I_3$	70.53	70.75
Benzyl	128.0–128.6[b]	44	$C_{14}H_9O_2I_3$	64.54	64.46
β-Phenylethyl	117.2–117.8	68	$C_{15}H_{11}O_2I_3$	63.05	63.36
γ-Phenyl-*n*-propyl	78.0–78.8[c]	52	$C_{16}H_{13}O_2I_3$	61.59	62.26

[a] Ethyl alcohol as solvent. [b] Granules. [c] Plates.

Experimental

To 1 g. of the acid chloride in a 10-cm. test-tube was added 0.5 cc. of the liquid alcohol or 0.5 g. of the solid alcohol and the mixture gently heated over a micro burner until the evolution of hydrogen chloride ceased. This usually required about ten minutes. The molten mass was then poured into 20 cc. of an ice and water mixture. Most of the esters solidified instantly. Those that came down as oils usually changed to solids in a few minutes, but in a few instances it was necessary to wash the oil with a 20% solution of alcohol to obtain a solid. One recrystallization will usually give a pure compound, but the results in Table I are from compounds which were recrystallized twice, with the exception of the ethyl and the 3-pentanol esters which were recrystallized three times. Either methyl or 95% ethyl alcohol can be used as a recrystallizing solvent. Methyl alcohol was used for the compounds in the table unless otherwise indicated. They crystallized in needles, unless otherwise noted. The isoamyl ester when crystallized from 95% ethyl alcohol sometimes came down as needles with the melting point shown and sometimes as plates with a melting point of 40.4–40.8°. The plates after melting, solidification and remelting had a melting point of 72.3–72.9°. When recrystallized from methyl alcohol, it always had the melting point of 72.3–72.9°. The melting points were all taken by Anschütz thermometers, which were checked against a thermometer with a Bureau of Standards certificate.

CHEMISTRY LABORATORY
BOSTON COLLEGE
CHESTNUT HILL 67, MASS.

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The Potassium Permanganate Test for Detection of Unsaturation[1]

BY V. N. IPATIEFF, W. W. THOMPSON[2] AND HERMAN PINES

Many books suggest for the detection of unsaturation (particularly in compounds insoluble in water) a procedure comprising treatment of an acetone solution of the compound dropwise with a 2% potassium permanganate solution, until the purple color of the permanganate persists.

It was found that such procedure gave a negative test for unsaturation with several olefinic compounds. The results with the various hydrocarbons tested were not consistent. For example, *β*-pinene showed a negative test for unsaturation, while *α*-pinene showed a positive test. It was found, however, that when the olefins showing a positive test were redistilled, the unsaturation test for olefins was negative. These results indicate that the olefins on standing might have undergone some changes, which caused the discoloration of the permanganate solution.

Absolute or 96% ethanol is a more suitable solvent for the unsaturation test; in the presence of olefins the color of the permanganate solution is

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[2] American Chemical Society Predoctoral Fellow (1947–1948).

discolored instantaneously. When a mixture of ethanol and acetone is used as a solvent, the rate of discoloration of the permanganate solution increases with the increase of alcohol concentration. Ethanol *per se* in the absence of olefins does not discolor the permanganate solution even after five minutes of standing. Methanol and 2-propanol act in a similar fashion as ethanol.

It was found that the addition of only a small amount of water to acetone increases the rate of discoloration when tested for unsaturation. A 5% solution of water in acetone seems to be a suitable solvent for the unsaturation test.

The procedure used for testing the various compounds was essentially as follows: One drop of a 2% aqueous solution of potassium permanganate was added to 0.1 cc. (0.1 g. if solid) of the compound dissolved in 2 cc. of the investigated solvent. Test was indicated as positive (+) when the color of the potassium permanganate changed within five seconds after the addition of the permanganate. If the potassium permanganate color persisted for longer than five minutes, the test was reported to be negative (−). The length of time required to discolorize the permanganate is expressed in seconds.

The tables summarize the results obtained.

TABLE I

COMPARISON OF ETHANOL WITH ACETONE IN PERMANGANATE TEST FOR UNSATURATION

	Solvents	
Compounds tested	Ethanol	Acetone
Amylenes	+	15 sec. (−)[a]
Octene	+	−
Butadiene	+	45 sec.
Cyclohexene	+	−
α-Pinene	+	−
3-Methylcyclohexene	+	−
1,1,3-Trimethyl-x-cyclohexene	+	30 sec. (−)[a]
β-Pinene	+	−
Dihydrolimonene	+	−
Limonene	+	−
Terpineol	+	180 sec.
Allyl alcohol	+	20 sec.
Cholesterol	−	−
Ergosterol	20	−
Mesityl oxide	+	+
Isophorone	+	20 sec.
Acetylacetone	20	240 sec.
Crotonic acid	+	10 sec.
Crotonaldehyde	+	+
Cholesteryl acetate	−	−
Dihydropyran	+	30 sec.

[a] Test after redistillation of the hydrocarbons.

TABLE II

EFFECT OF MIXTURES OF ETHANOL/ACETONE ON RATE OF PERMANGANATE TEST OF OLEFINS

Alcohol concentration, vol. %	100	80	60	40	20	0
Compounds tested	Time in seconds for color change					
Limonene	0	5	15	30	60	>300
Cyclohexene	0	5	15	40	120	>300
Methylcyclohexene	0	10	30	90	240	>300

THE IPATIEFF HIGH PRESSURE
AND CATALYTIC LABORATORY
DEPARTMENT OF CHEMISTRY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

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Hydrolytic Titrations of Lead with Potassium Cyanide

BY LOUIS MEITES

In the course of a study of hydrolytic titrations of various divalent cations with potassium cyanide, it was found that the atypical behavior of plumbous ion was of particular interest. It is well known that most such titrations are characterized by a continuous rise in *p*H on addition of cyanide, with sharp increases at points corresponding to quantitative formation of insoluble compounds, such as $M(CN)_2$, or complex ions, such as $M(CN)_4^=$.

Titration of an aqueous solution of lead nitrate, however, gives, after an ill-defined end-point at about 1.5 mole of cyanide per mole of lead, a sharp downward break in *p*H at a mole ratio of about 1.8. This break is of the order of 0.25 *p*H unit, and it is followed by a steady rise in *p*H as the titration is continued, with no clear indication of any further end-point to a mole ratio of at least eight.

In 50% ethanol a pronounced end-point (taken as the point of maximum slope) is observed at a mole ratio of 1.002 ± 0.004, and it is followed by, first, a downward break similar to that found in aqueous medium, and then, at a mole ratio of 1.50 ± 0.01, a second sharp end-point.

The insoluble products of the reactions in 50% ethanol were isolated by titrating 500-ml. portions of an 0.05 *M* solution of lead nitrate with standard potassium cyanide until the previously determined *p*H values at the respective end-points, as measured with a Beckman glass electrode *p*H meter, had been exactly reached. The products were filtered off, washed with 50% ethanol and ether, and air-dried. They were analyzed by decomposition in platinum over a very low flame, followed by ignition at a dull red heat, and both gave light yellow plumbous oxide apparently uncontaminated by any trace of a red higher oxide. The compound formed at the first end-point evolved much nitrogen dioxide during its decomposition. Found: PbO, 78.1, 78.2; calculated for $Pb(OH)(NO_3)$, 77.99%. The other compound gave off only a faint odor of cyanogen. Found: PbO, 87.4, 87.3; calculated for $Pb(OH)(CN)\cdot Pb(CN)_2$, 87.62%. This substance has not previously been described in the literature.

The reactions taking place during this titration may, therefore, be represented by the equations

$$Pb^{++} + CN^- + H_2O + NO_3^- \longrightarrow Pb(OH)(NO_3) + HCN \quad (1)$$