[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

A Method of Distinguishing Primary, Secondary and Tertiary Aliphatic Acids

BY FRANK C. WHITMORE AND HARRY M. CROOKS, JR.

Whitmore and Laughlin[1] found that when certain aliphatic acids were treated with phosphorus pentoxide at temperatures in the neighborhood of 150° the relative yields of carbon monoxide and carbon dioxide were dependent upon the character of the alkyl group attached to the carboxyl carbon. Their results indicated this as a possible method of distinguishing between primary, secondary and tertiary acids RCH_2COOH, $RR'CHCOOH$ and $RR'R''CCOOH$. In the present study this has been confirmed and extended to cover fifteen aliphatic acids other than those reported by Whitmore and Laughlin. The studies have included six primary acids, eight secondary acids and five tertiary acids.

In the case of primary acids, the gaseous products totaled 5–13% of the theoretical amount required by complete loss of the carboxyl group, the ratio of carbon dioxide to carbon monoxide increasing, with increase in molecular weight of the acid, from 5:1 to a 13% yield of carbon dioxide with no carbon monoxide. With secondary acids, the yield of carbon monoxide increased from 9 to 30% and the yield of carbon dioxide decreased from 1.7 to 0.5% with increase in molecular weight of acid. With tertiary acids, the carbon monoxide yield increased from 55 to 90% with increase in molecular weight of acid, only traces of carbon dioxide being formed.

A method for distinguishing between secondary and tertiary acids is especially important in view of the confusion about the two acids, $C_{11}H_{23}CO_2H$, obtained by the oxidation of triisobutylene.[2] From their speeds of esterification they were thought to be tertiary although one later was proved to be secondary. The present method distinguishes them definitely, the dineopentylacetic acid forming 30% CO and 0.5% CO_2 while the isomeric methyl-*t*-butylneopentylacetic acid gives 90% CO and 0.2% CO_2.

All reactions were run at the same temperature (155–160°). The yield of gas is probably dependent on this factor. Thus, Kipping[3] obtained 30–60% yields of ketone and presumably a corresponding yield of carbon dioxide, by treating primary acids with phosphorus pentoxide at 200–220°.

In all cases, a heavy tar was formed in the reaction.

Experimental

The apparatus used consisted of a three-necked, 200-cc., round-bottomed flask fitted with a gas inlet tube, a dropping funnel and a reflux condenser. Gases from the reaction were led through the condenser to a calibrated gas collecting carboy. The system was so assembled that all parts could be flushed out with nitrogen. In the case of acids solid at room temperature a procedure was devised permitting introduction of the solid in small portions without opening the system.

Gas analyses were made with a standard Orsat apparatus using 10% sodium hydroxide solution for carbon dioxide and cuprous chloride in hydrochloric acid for carbon monoxide.

Procedure.—Approximately one-tenth mole runs of each acid were made. For this, 25 g. of phosphorus pentoxide was weighed into the reaction flask, the acid placed in the dropping funnel, the apparatus assembled and tested for leaks. The apparatus was then swept out with from three to five liters of dry nitrogen with the gas-collecting carboy disconnected. The carboy was connected and the bath surrounding the flask heated to 100–110°. The acid was then added slowly (about forty minutes for 0.1 mole) to the hot oxide. After all the acid was added the bath temperature was raised to 155–160° and held at that point

DESCRIPTION OF ACIDS USED

Acid	B. p.		$n^{20}D$	Source
	°C.	Mm.		
n-Caproic	114	740	1.4163	Mallinckrodt Chem. Wks.
Isocaproic			1.4150	Eastman Kodak Co.
t-Butylacetic	96	25	1.4107	[a]
Methylneopentylacetic	119	20	1.4242	[a]
n-Caprylic			1.4280	Eastman Kodak Co.
Stearic	U.S.P.X.			Baker Chemical Co.
Diethylacetic	119	731	1.4132	[b]
Methyl-*n*-propylacetic	191	735	1.4140	[b]
Diallylacetic	113	11	1.4520	[c]
Di-*n*-propylacetic	120	16	1.4239	[d]
Di-*n*-butylacetic	143	16	1.4328	[d]
Dineopentylacetic	m. p. 88–89°			[d]
Trimethylacetic	m. p. 35°			[e]
Ethyldimethylacetic	100	23	1.4141	[c]
Diethylmethylacetic	134	50	1.4250	[e]
Triethylacetic	m. p. 39°			[e]

[a] From oxidation of diisobutylene; to be published later. [b] From Dr. F. A. Karnatz, this Laboratory; malonic ester synthesis. [c] From Dr. D. M. Jones, this Laboratory. [d] From Dr. P. A. Lasselle, this Laboratory; hydrolysis of corresponding nitriles. [e] Addition of carbon dioxide to corresponding Grignard compound.

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[1] Whitmore and Laughlin, THIS JOURNAL, **54**, 4462 (1932).

[2] Conant and Wheland, *ibid.*, **55**, 2499 (1933); Whitmore and Laughlin, *ibid.*, **56**, 1128 (1934); Whitmore and Wilson, *ibid.*, **56**, 1397 (1934).

[3] Kipping, *J. Chem. Soc.*, **57**, 532, 980 (1890); **63**, 452 (1892).

for an hour to ensure complete reaction. During this time the mass in the reaction flask became black and gummy.

The flask was allowed to cool to room temperature and then the excess of pentoxide was hydrolyzed by adding 30–60 cc. of water through the dropping funnel (air excluded). When hydrolysis was completed, the gaseous contents of the flask were swept into the carboy with 2 liters of dry nitrogen and the total gas analyzed for carbon dioxide and carbon monoxide.

The results are given in tabular form. The data for *n*-butyric, isobutyric, trimethylacetic and methyl-*t*-butylneopentylacetic acids, determined previously,[1,4] were included for purposes of comparison.

Acid	% CO	% CO_2
Primary		
n-Butyric	1.1	5.5
n-Caproic	0.9	6.3
Isocaproic	.8	.77
t-Butylacetic	.5	5.3
n-Caprylic	.14	9.9
Stearic	.0	13.0
Secondary		
Isobutyric	8.8	1.7
Diethylacetic	26.0	1.6
Methyl-*n*-propylacetic	21.7	1.6
Di-*n*-propylacetic	27.5	0.6
Diallylacetic	17.6	.5
Di-*n*-butylacetic	24.6	.5
Methylneopentylacetic	26.6	.8
Dineopentylacetic	30.0	.5
Tertiary		
Trimethylacetic	55.0	0.2
Ethyldimethylacetic	68.0	.0
Diethylmethylacetic	84.5	.6
Triethylacetic	77.5	.0
Methyl-*t*-butylneopentylacetic	90.0	.2

Summary

Fifteen aliphatic acids have been treated with phosphorus pentoxide at 150–160° and the yields of carbon monoxide and carbon dioxide recorded.

On the basis of the yield and composition of the gaseous products of this reaction a method of discriminating between acids having a primary, secondary or a tertiary alkyl group attached to the carboxyl carbon is proposed.

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[4] Whitmore and Laughlin, THIS JOURNAL, **56**, 1128 (1934).

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Studies on Phenothiazine. IV. Potentiometric Characterization of Thionol

BY FLOYD DEEDS AND C. W. EDDY

In a previous report[1] we have described a simple method for the conversion of phenothiazine to thionol (hydroxyleucophenthiazone). We have pointed out that thionol is a reversible oxidation–reduction system and reported the potential of the system under conditions when the ratio of the concentration of the oxidant to the concentration of the reductant was unity. This paper is concerned with details of the potentiometric studies of the system thionol–leuco thionol.

All oxidation–reduction potentials were measured with bare platinum electrodes, the saturated calomel half cell being used as the working standard of reference. Two platinum electrodes were used in each measurement and no potential reading was accepted as final until the two electrodes agreed within 0.1 mv. when the system was well poised. When the concentration of one component was low relative to that of the other, a discrepancy of not more than 0.5 mv. was considered indicative of equilibrium. Before using the electrodes they were cleaned in aqua regia, washed thoroughly, and their behavior checked in 0.001 *M* ferri–ferrocyanide solution in which the concentration of oxidant and reductant was equal. All potentials were measured with a Leeds and Northrup type K potentiometer placed in the grid circuit of a General Electric FP 54 tube as shown in the accompanying diagram.

Measurements were made in an air-bath at a temperature of 21–22°. Potentials were measured in an atmosphere of pure nitrogen which was passed over heated copper gauze to remove all traces of oxygen. The leuco base of thionol was prepared by reduction of thionol with platinized asbestos and a stream of hydrogen freed of oxygen by passage over heated platinized asbestos. When reduction was completed the solution of leuco base was freed of hydrogen with a stream of oxygen-free nitrogen. The stream of nitrogen also served to force the solution of leuco thionol through a sintered glass filter to remove the asbestos and to transfer the solution to an oxygen-free buret. Since the measured amount of solution of oxidant (10 cc.) placed in the titration vessel and the solution treated for reduction to the leuco base were aliquots of the same thionol solution, the ratio of oxidant to reductant after each addition of reductant from the buret was determined readily.

For the determination of the curve relating the potential to the ratio of reductant to oxidant a solution of thionol

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[1] F. DeEds and C. W. Eddy, THIS JOURNAL, **60**, 1446 (1938).