A New Procedure for the Duclaux Method

BY JAMES B. MCNAIR

Up to the present time no method is available which will give reliable results for the analysis of four volatile aliphatic acids by the Duclaux method. It has been found by the writer that the quantitative analysis by a chemical method of one of the four acids in the Duclaux distillate makes possible the reliable estimation of the remaining three acids by the Duclaux method. In fact the quantitative estimation of one or more acids by an accurate chemical method increases the accuracy of the results of the Duclaux method when a mixture of three or more acids is involved. In the following paper a brief outline of the new procedure will be illustrated by an example.

In the new procedure for calculating the results of an analysis of mixtures of four volatile acids, one or more acids are determined quantitatively by chemical methods and the remainder of the acids may be determined quantitatively by Gillespie and Walters' graphic method.[1]

The following acids have been used: formic acid 98–100% m. p. 6–8°, acetic acid 99.9% m. p. 16.6°, propionic acid b. p. 140–142° and *n*-butyric acid b. p. 161–163°, all obtained from high grade firms.

In mixtures of these four acids, formic acid may be determined by the mercuric chloride method,[2] acetic because of its resistance to oxidation may be determined by the Macnair method,[3] and propionic in the presence of acetic and formic only, by the oxalate method.[4]

For example, a mixture of 7.90 cc. of 0.1 *N* formic, 5.35 cc. of 0.1 *N* acetic, 4.90 cc. of 0.1 *N* propionic and 9.88 cc. of 0.1 *N* butyric acids is taken for analysis. One or more Duclaux distillations are made with the mixture, and the formic acid is determined either in the distillate or in the residue in the distilling flask by the mercuric chloride method.

The amount of formic acid in the Duclaux distillate and distillate residue is determined by the mercuric chloride method. It is found to be equal to 7.38 cc of 0.1 *N*. In Table I it is shown that 61.6% of the total formic acid comes over in the distillate. This amounts to 7.38 × 0.616 = 4.55 cc. of 0.1 *N*. This quantity of formic acid is subtracted from the original titer figure of the distillate, Table III; 23.30 − 4.55 = 18.75 cc. of 0.1 *N*.

The remainder, 18.75 cc., which consists of all the other acids except formic, is now used like the original distillate titer figure of an unknown distillate. The entire procedure is perhaps made more clear by the accompanying Table III. Let *M* represent the acid most volatile with

---

[1] Gillespie and Walters, THIS JOURNAL, **39**, 2027–2055 (1917).

[2] Association of Official Agricultural Chemists, "Official and Tentative Methods of Analysis," 2d ed., 1925, Washington, D. C.

[3] D. S. Macnair, *Chem. News*, **55**, 229 (1887); Fresenius, *Z. Anal. Chem.*, **27**, 398 (1888).

[4] McNair, THIS JOURNAL, **54**, 3249–3250 (1932).

TABLE I

THE AMOUNTS OF THE VARIOUS ACIDS TO BE FOUND IN THE DUCLAUX DISTILLATE (GILLESPIE, WALTERS AND MCNAIR)

Distillate, cc.	Formic acid, cc.	Acetic acid, cc.	Propionic acid, cc.	Butyric acid, cc.
10	3.4	6.4	11.2	16.4
20	7.3	13.0	22.2	31.2
30	11.5	19.7	32.7	44.8
40	16.1	26.7	42.9	56.6
50	21.3	34.1	52.7	67.3
60	26.6	41.6	62.0	76.2
70	33.0	49.9	70.9	84.0
80	40.5	58.7	79.1	90.1
90	49.6	68.7	86.7	94.8
100	61.6	79.9	93.6	97.8

TABLE II

PERCENTAGES OF TOTAL ACID CONTAINED IN 100 CC. OF DUCLAUX DISTILLATE (GILLESPIE AND WALTERS)

Distillate, cc.	Formic acid	Acetic acid	Propionic acid	Butyric acid
10	6.5	8.0	12.0	16.7
20	13.0	16.3	23.7	31.9
30	20.2	24.6	34.9	45.7
40	27.8	33.5	45.8	57.9
50	35.9	42.7	56.3	68.8
60	44.8	52.1	66.2	77.9
70	55.2	62.4	75.7	85.8
80	66.8	73.4	84.5	92.1
90	81.2	85.7	92.6	96.8
100	100.0	100.0	100.0	100.0

steam, I the intermediate, and L the least volatile with steam. In this example, $M = B$, or butyric, $I = P$, or propionic, and $L = A$, or acetic. Calculations are performed as indicated in Table III. In this table $B-R$ is the percentage of butyric acid contained in the various fractions of the Duclaux distillate, as indicated in Table II, less the figures under R in the preceding column in Table III. Similarly $B-A$ is butyric minus acetic and is obtained in a like manner from Table II; $B-P$ is determined in the same way. $(B-P)/(B-A)$ is $(M-R)/(M-L)$ when it is assumed that the mixture is one of B, P, and A.

It is now assumed that the mixture is $B + P + A$. $(B-P)/(B-A)$ and $(B-R)/(B-A)$ from Table III are plotted on graph paper as in Fig. 1. The first point is ignored in the calculations as the error in this, caused presumably by carbon dioxide, is too great. The figure shows in this instance that $l + i = 0.40$, $l = 0.28$, or 28%, the fraction of acetic acid in 100 cc. of distillate; therefore $i = 0.12$, that is, 12% intermediate acid = propionic in 100 cc. of distillate. Now M, the fraction of butyric acid in 100 cc. of distillate $I-(l + i) = I-0.40 = 0.60$.

TABLE III

DERIVATION OF THE VALUES USED IN FIGURE 1

Distillate, cc.	Titer cc. of 0.1 N	Formic acid,[a] cc. of 0.1 N	Other acids, cc. of 0.1 N	R[b] Table II	$B - R$	$B - A$	$\frac{B-R}{B-A}$	$\frac{B-P}{B-A}$
10	2.95	0.25	2.70	14.40	3.20	9.67	0.331	0.564
20	5.60	.54	5.06	26.99	5.99	17.08	.351	.551
30	8.15	.85	7.30	38.93	7.71	22.34	.345	.531
40	10.60	1.19	9.41	50.19	8.55	25.61	.334	.514
50	12.90	1.57	11.33	60.43	8.95	25.76	.348	.526
60	15.05	1.97	13.08	69.76	8.94	26.77	.334	.474
70	17.10	2.44	14.66	78.19	8.04	23.99	.335	.449
80	19.12	2.99	16.13	86.03	6.29	18.92	.332	.429
90	21.15	3.66	17.49	93.28	3.66	11.24	.325	.395
100	23.30	4.55	18.75	99.99				

[a] Determined by $HgCl_2$ and Table I (see text). [b] Percentages of residual acid (other acids besides formic) contained in 100 cc. of the Duclaux distillate, calculated as in Table II.

TABLE IV

THE RESULTS OF ANALYSES OF HIGH AND LOW PERCENTAGE MIXTURES OF FORMIC, ACETIC, PROPIONIC AND BUTYRIC ACIDS EXPRESSED IN CC. OF 0.1 N ACID

Taken					Found					Errors				
F	A	P	B	Total	F	A	P	B	Total	F	A	P	B	Total
2.64	2.82	3.46	2.62	11.54	2.74	2.18	3.66	2.31	10.89	0.1	−0.64	0.20	−0.31	−0.65
2.26	3.00	3.24	3.58	12.08	2.14	2.76	3.60	3.40	11.90	− .12	− .24	.36	− .18	− .18
6.95	8.25	16.17	8.41	39.78	6.94	7.43	17.25	7.86	39.48	− .01	− .82	1.08	− .55	− .30
5.27	8.65	9.80	8.10	31.82	5.30	8.20	10.34	8.18	32.02	.03	− .45	0.54	.08	.20

Now, there is 18.75 cc. of 0.1 N as the total acid in 100 cc. of distillate. In this there is

$$\begin{aligned} l &= 0.28 \times Q_{100} = 5.250 \text{ cc. of acetic} \\ i &= 0.12 \times Q_{100} = 2.250 \text{ cc. of propionic} \\ m &= 0.60 \times Q_{100} = 11.250 \text{ cc. of butyric} \\ Q_{100} &= 18.75 \text{ cc. of } 0.1\ N \text{ (other acids than formic)} \end{aligned}$$

$I/0.7784 = 1.285$ acetic acid in the original 110 cc., since 77.84 is the percentage of acetic acid coming over in 100 cc. of distillate (Table I).

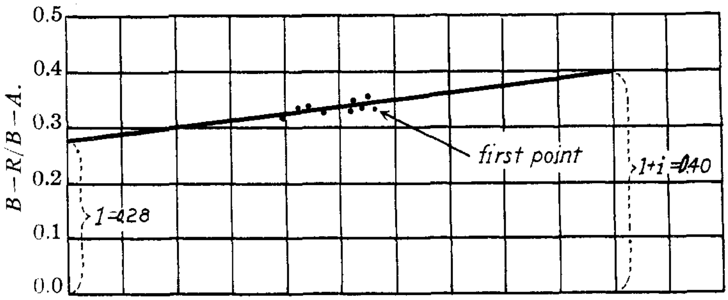

Fig. 1.

$I/0.9508 = 1.052$ propionic acid in the original 110 cc., since 95.08 is the percentage of propionic acid coming over in 100 cc. of distillate (Table I). $I/0.9774 = 1.023$ butyric acid in the original 110 cc., since 97.74 is the percentage of butyric acid coming over in 100 cc. of distillate (Table I).

	Found, cc. of 0.1 N	Present, cc. of 0.1 N	Error, cc. of 0.1 N
$x = 1.285 \times 5.25 =$	6.75 acetic	5.35	+1.40
$y = 1.052 \times 2.25 =$	2.37 prop.	4.90	−2.53
$z = 1.023 \times 11.25 =$	11.51 butyr.	9.98	+1.63
	7.38[5] formic	7.91	−0.53[5]
Total	28.01	28.04	−0.03

Better accuracy could have been attained by taking special precautions with the technique throughout. The above, however, serves to illustrate the new procedure. Details as to the method and calculations may be found in Gillespie and Walters' paper referred to above, to the senior author of which the present writer desires to acknowledge assistance with the calculations involved.

The results of the analyses of high and low percentage mixtures of formic, acetic, propionic and butyric acids are shown in Table IV.

Use of the Duclaux Method for Unknown Mixtures.—When more than four acids are present in significant quantities, more than one acid must be

---

(5) This should be 7.83 and the error should be therefore 0.08 cc.

determined chemically or the solution must be fractionated into mixtures containing only four acids in significant quantities before applying the Duclaux method. If necessary, the acids may be freed partially from their salts and distilled, as suggested by Liebig[6] and Gillespie and Walters.[1]

To use the Duclaux method most successfully, the acids met with should be identified qualitatively before calculating the results. The tests suggested by Agulhon and rearrangement by Dyer seem the most practicable. These tests depend upon the relative solubility of the iron and copper salts of the fatty acids in various organic solvents.[7]

Summary

A new procedure has been outlined, illustrated by an example, for the estimation of four acids by the Duclaux method. In the new procedure one or more acids are determined quantitatively by chemical methods and the remainder determined by the Duclaux method.

(6) Liebig, *Ann.*, **71**, 355 (1849).

(7) *J. Biol. Chem.*, **28**, 445–473 (1917).

RECEIVED JUNE 11, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Conductivity of Grignard Reagents in Ether Solutions

BY W. V. EVANS AND F. H. LEE

The conductivity of the Grignard reagent in ether solutions has been studied by numerous investigators. Kondyrew and Manojew[1] measured the conductivity of ethylmagnesium bromide at various temperatures. Kondyrew and Ssusi[2] studied the effect of dilution on the conductivity of ethylmagnesium iodide and postulated the formation of complex organic compounds at certain concentrations. Recently Dufford and his coworkers[3] investigated the effect of light on the conductivity of these solutions. In the present work we have extended this investigation to several other Grignard compounds.

Experimental

Preparation of Solutions.—Pure dry alkyl or aryl bromide was mixed with ether and added to dry magnesium turnings in slight excess of the amount necessary for the reaction $RX + Mg = RMgX$. After reaction the flask was heated for two hours on a water-bath. All precautions were taken against the entrance of air and moisture.

Measurement of Conductivity.—The conductivities of ethylmagnesium bromide, benzylmagnesium bromide, *n*-butylmagnesium bromide, phenylmagnesium bromide, and magnesium bromide have been measured at 20, 0 and −10°. The solubility of magnesium bromide in ether is so small that only the conductivity of dilute solutions of

---

(1) Kondyrew and Manojew, *Ber.*, **58**, 464 (1925).

(2) Kondyrew and Ssusi, *ibid.*, **62**, 1856 (1929).

(3) Dufford, *Phys. Rev.*, **35**, 998 (1930); *J. Phys. Chem.*, **34**, 1544 (1930).