284 g. of the desired ketone was obtained; b. p. 128° (5 mm.); n^{20}_D 1.5330; d^{20}_4 0.9819. This represents a yield of 75%.

Anal. (semi-micro) Calcd. for $C_{13}H_{16}O$: C, 82.92; H, 8.57. Found: C, 82.61; H, 8.46.

Condensation of Mesityl Propenyl Ketone with Ethyl Oxalate.—A total of 6.5 g. of finely cut potassium was placed in a flask with 45 cc. of dry ether. Absolute alcohol (29 cc.) was added, with shaking, to convert the potassium to potassium ethoxide.

To the ether solution was then added 12.2 g. of ethyl oxalate dissolved in 15 cc. of ether. Fifteen minutes later, 15.7 g. of mesityl propenyl ketone dissolved in 15 cc. of ether was added, with continued shaking. The color of the solution soon changed to a dark red. The mixture was allowed to stand for a period of twenty hours in an ice box.

The solution was then treated with water and neutralized with acetic acid. The ether layer was separated and dried. Evaporation of the solvent left a crystalline mass. Crystallization from alcohol gave 22 g. of beautiful light yellow crystals which melted, with decomposition, at 156°; yield 90%.

Anal. (micro) Calcd. for $C_{17}H_{20}O_4$: C, 70.78; H, 6.99. Found: C, 70.74; H, 6.96.

Oxidation with Hydrogen Peroxide.—One gram of the ester was placed in a flask with 20 cc. of 10% sodium hydroxide solution and 100 cc. of 3% hydrogen peroxide solution. The mixture was allowed to stand for a period of twelve hours at room temperature.

The solution was then acidified with acetic acid. The precipitate which formed was collected on a filter and redissolved in alkali. It was then thrown out of solution again by the addition of more acetic acid. Recrystallization from a mixture of benzene and low-boiling petroleum ether gave 0.34 g. of beautiful colorless crystals of β-isodurylic acid; m. p. 152°.

Summary

Phenyl propenyl ketone (I) has been prepared from crotonyl chloride and benzene by use of Friedel–Crafts synthesis. The ketone was condensed with ethyl oxalate in ether solution, potassium ethoxide being employed as a catalyst.

The potassium salt (II) was converted into the benzoate (III) by treatment with benzoyl chloride. When the salt was acidified with acetic acid, the free keto ester (IV) was produced.

Mesityl propenyl ketone (V) has been prepared in an analogous manner. It was, likewise, condensed with ethyl oxalate, producing a keto ester (VI).

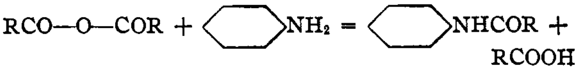
URBANA, ILL. RECEIVED OCTOBER 5, 1936

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS & COMPANY]

Quantitative Determination of Anhydrides of Carboxylic Acids

BY DONALD MILTON SMITH AND W. M. D. BRYANT

Organic acid anhydrides ordinarily are estimated analytically either by hydrolysis followed by titration of both acidic groups, or by the use of a reaction which converts one acidic residue into a neutral substance leaving only one carboxyl as a measure of the anhydride present. While both analytical schemes are bases of accepted methods, it is apparent that neither alone is sufficient to differentiate sharply between anhydrides and free acids. However, by using the two principles in combination, it becomes possible to determine the -CO-O-CO- content of a mixture, even though the exact nature and composition of the mixture is unknown. Radcliffe and Medofski[1] have made a careful investigation of the above-mentioned procedures as applied to acetic anhydride. The majority of these procedures make use of the fact that an anhydride reacts with aniline to form a mole each of anilide and acid, respectively[2]



$$RCO{-}O{-}COR + C_6H_5NH_2 = C_6H_5NHCOR + RCOOH$$

The action of alcoholates of the alkali metals upon anhydrides is analogous to that of aniline, a mole of ester and a mole of alkali salt resulting from the reaction carried out as a titration.[3]

Except for the closely related work of Holde[4] on the titration of higher fatty acid anhydrides with alcoholic sodium hydroxide, little use has been made of the above reaction in an analytical way.

In the present investigation a standard solution of sodium methylate was used in place of aniline,

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(1) Radcliffe and Medofski, *J. Soc. Chem. Ind.*, **36**, 628 (1917).

(2) Menschutkin and Vasiliev, *J. Russ. Phys.-Chem. Soc.*, **21**, 190 (1889).

(3) Caudri, *Rec. trav. chim.*, **48**, 778 (1929).

(4) Holde and Smelkus, *Ber.*, **53**, 1889 (1920); Holde and Tacke, *ibid.*, **53**, 1898 (1920).

since it offered the advantage of combining into a single step the cleavage and neutralization processes of the older method while sharing its high reactivity. Total acidity was determined on a separate sample by titration with aqueous sodium hydroxide. In this connection it was found that the addition of a large amount of pyridine just before titration greatly accelerated the hydrolysis of anhydrides rendering it in most cases instantaneous. The two basic reactions involved are

$$\mathrm{RCO{-}O{-}COR + CH_3ONa = RCOOCH_3 + RCOONa} \tag{1}$$

and

$$\mathrm{RCO{-}O{-}COR + 2NaOH = 2RCOONa + H_2O} \tag{2}$$

It is readily apparent that in mixture with other acidic materials the distinctive measure of anhydride present is the amount of acyl radical rendered unavailable as ester, or the equivalent difference between the titers of the above reactions. The initial presence of free acids is without effect upon this determination.

A group of ten anhydrides selected for wide differences in structure were analyzed by this method with an average precision of ±0.2%. The method is stoichiometric within this limit as shown by results obtained with glutaric, phthalic and camphoric anhydrides, the substances obtained in the highest purity. All of the compounds except camphoric anhydride were titrated directly in the cold. Due to steric hindrance arising from the presence of an adjacent tertiary carbon atom, the latter material required thirty minutes of heating at 60° with an excess of reagent, followed by back-titration with standard acid. The analytical data are given in Table I.

TABLE I

ANALYTICAL DATA FOR ANHYDRIDES

Anhydride	Millimoles per gram sample NaOH (a)	 NaOCH$_3$ (b)	 -CO-O-CO- (a-b)	% of theoretical -CO-O-CO-
Acetic	19.61	9.88	9.73	(4)[a] 99.3 ± 0.2
Propionic	15.40	7.79	7.61	(3) 99.0 .2
n-Heptylic	8.21	4.21	4.00	(1) 96.9
Succinic	19.83	10.35	9.48	(4) 94.8 .2
Maleic	20.20	10.22	9.98	(2) 97.8 .0
Glutaric	17.42	8.67	8.75	(2) 99.8 .1
Camphoric	10.99	5.49	5.50	(2) 100.2 .4
Benzoic	8.84	4.45	4.39	(2) 99.3 .1
Phthalic	13.50	6.75	6.75	(2) 99.9 .3
Furoic	9.61	4.97	4.64	(4) 95.6 .2

[a] Figures in parentheses indicate number of individual determinations.

The matter of interfering substances was also investigated and as the probable titration behavior of lactones was in doubt several examples of this class were examined and the results recorded in Table II. Ordinary esters and stable lactones like phthalide and coumarin are inert toward the reagents as ordinarily employed, hence do not interfere. Readily hydrolyzed compounds of these classes such as alkyl formates and glucono-δ-lactone although unaffected by sodium methylate undergo hydrolysis in aqueous solution and so lead to ambiguous results in mixtures. β-Methylumbelliferone, a substituted coumarin, reacts as an acid with both reagents, hence does not affect the determination of anhydrides.

TABLE II

ANALYTICAL DATA FOR LACTONES

Lactone	Millimoles per gram sample NaOH (a)	 NaOCH$_3$ (b)	 Δ (a−b)
Glucono-δ-lactone	5.65	0.05	5.60
Phthalide[a]	0.11	.02	0.09
Coumarin	.05	.02	.03
β-Methylumbelliferone	5.63	5.62	.01

[a] Obtained from British Drug House, Ltd.; remaining lactones Eastman products.

Experimental

Compounds Investigated.—With two exceptions all of the anhydrides studied in the present research were Eastman products, and were used without further purification. **Phthalic anhydride** ("Aero" Brand) was obtained from American Cyanamide and Chemical Corp., and **glutaric anhydride** was prepared from the acid by the method of Mol.[5] In this connection, evidence was obtained that solid anhydrides adsorb large quantities of water vapor on short exposure to moist air. Decomposition is not instantaneous but takes place to a serious extent during subsequent storage. To minimize this difficulty, samples for analysis were dispensed by means of a simple "dry manipulator."

Analytical Procedure

One to three grams of sample is weighed into a dry 250-cc. g. s. volumetric flask (calibration unnecessary) or similarly designed vessel. If the sample is a solid, 20 to 30 cc. of dry methanol or acetone is added, warming if necessary to complete solution. The solution is then titrated directly with 0.5 *N* sodium methylate in methanol to a phenolphthalein or thymol blue end-point. The indicator should be made up in dry dioxane or acetone (an alcohol solution would be unsuitable for use in the next step). This titer is a measure of the anhydride plus any free acid present.

A second weighed sample is mixed with 25 cc. of C. P. pyridine and titrated with 0.5 *N* aqueous sodium hydroxide to the indicator previously employed. Alcohol should be omitted in order to avoid ester formation. This titer is a measure of the total acidity of the sample. The true anhydride content is measured by the difference between the two titers expressed in moles per gram of sample.

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[5] Mol, *Rec. trav. chim.*, **26**, 373 (1907).

The sodium methylate solution is prepared by dissolving the required amount of metallic sodium in dry c. p. methanol. Although precautions should be taken to keep the solution dry, the presence of up to 1% of water introduces only a small error. The two alkalies should be compared frequently with standard 0.5 *N* acid. Anhydrides that are unreactive because of steric hindrance, may be heated with an excess of either alkali and back titrated cold with standard acid. In such cases, however, esters must be absent to avoid interference. Camphoric anhydride was the sole example of this class encountered.

Summary

1. A rapid and precise method for the determination of anhydrides of carboxylic acids based on sodium methylate titration has been developed. The method has been applied successfully to the following anhydrides: acetic, propionic, *n*-heptylic, succinic, glutaric, maleic, camphoric, benzoic, phthalic and furoic.

2. In connection with the above method, the hydrolytic cleavage of anhydrides was found to be accelerated by the use of pyridine.

3. The interference of lactones has been investigated. Phthalide and coumarin do not react. β-Methylumbelliferone reacts but does not interfere. Glucono-δ-lactone interferes with anhydride determinations.

Wilmington, Del. Received October 7, 1936

[Contribution from the Kedzie Chemical Laboratory, Michigan State College]

The Surface Tensions, Densities, Free Surface Energies and Parachors of Some Derivatives of Benzylated Phenols[1]

By D. T. Ewing and Frances W. Lamb

In this paper data are presented for the measurement of the surface tension and density at different temperatures of a series of new organic compounds, which are derivatives of benzylated phenols. From these values the molal free surface energy and parachors have been calculated. Although these physical factors have been evaluated for a number of organic compounds, reliable surface tension values of only four diphenyl and two triphenyl compounds have been reported previously.

The compounds used in these investigations were those prepared by R. C. Huston and associates in a series of investigations in this Laboratory. These substances were found to be of sufficient purity to warrant direct measurement without further purification. In each case the compounds had been carefully distilled many times.

Density measurements were made at different temperatures with a pycnometer which was essentially a bulb of glass blown on a capillary. A special pycnometer was made partly because in several cases the sample of liquid was limited to a few ml. and partly because the best density bulb is one which is spherical in form with only a fine capillary opening. In each case the pycnometer was carefully calibrated with water at the several temperatures. Density measurements were made at 25, 35 and 50°. For this purpose the substances were equilibrated in constant-temperature water-baths which did not vary in temperature more than 0.005°.

Surface tension measurements were made with a metal drop weight apparatus[2] supported on a heavy concrete pillar free from the floor of the laboratory to avoid any vibration. The radius of the tip was carefully determined with a Gaertner comparator and found to have a value of 0.26740 cm. The drop weight assembly with the liquid was lowered below the surface of the water in the thermostat and allowed to remain until the temperature of the liquid was a constant when the drop weight determinations were made. For each liquid, when the volume available permitted, 25 to 30 drops were formed very slowly into a weighing bottle and from this weight that of the drop was determined.

From the weight of the drop and the density of the liquid the surface tension γ was calculated by the equation

$$\gamma = \frac{mg}{2\pi r f(r/v^{1/3})}$$

where m = mass of drop in grams
g = 981 dynes
r = 0.26740 cm. the radius of the tip
v = volume of the drop

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[1] A portion of Part I of a thesis submitted to the Graduate Faculty of the Michigan State College by Miss Frances W. Lamb in partial fulfilment of the requirements for the Ph.D. degree, June, 1933.

[2] Harkins and Brown, This Journal, **41**, 519 (1919)