[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

Levulinic Acid. IV. The Vapor Pressures of its Normal-Alkyl Esters (C_7-C_{10})

BY MILFORD A. COWLEY AND H. A. SCHUETTE

In an earlier study[1] of the temperature-vapor pressure relationships of an homologous series of alkyl esters of levulinic acid, questions arose concerning the preparation and the stability of its higher members in the region of their boiling points. In order to obtain more information about members of this series and to test the validity of a formula, at that time presented, for calculating the specific gravities of the normal alkyl esters, the *n*-heptyl, *n*-octyl, *n*-nonyl and *n*-decyl esters were prepared and certain of their simpler physical properties determined as before. Because the work has been temporarily halted, it seems desirable to record now the data that have been obtained.

Experimental

Preparation of the Esters.—Levulinic acid (n^{40} 1.4342) was directly esterified with the appropriate alcohol[2] (molecular ratio of acid to alcohol, 1.1 to 1) using as a catalyst hydrogen chloride in the amount of 3% of the weight of the alcohol. Carbon tetrachloride served the dual role of solvent for the reactants and of agent for the removal of water from the reaction mixture by means of a continuous separator. Although the higher alcohols themselves are sufficiently insoluble in water to make possible their use as separating agents, such procedure is undesirable because of the high boiling temperature of the alcohols and the inevitable waste of such valuable reagents.

As was previously found in the cases of the *n*-amyl and *n*-hexyl esters, complete separation of the higher esters from the excess levulinic acid was not accomplished by a single fractional distillation under reduced pressure. Satisfactory removal of the acid from the ester fraction of the first distillation was brought about by shaking the mixture with dry, powdered sodium carbonate (6 to 8 g. of Na_2CO_3 to 50 g. of ester). Water was added dropwise with thorough shaking after each addition. The close approach of neutrality was indicated when the sodium carbonate particles agglomerated and settled as a granular mass. Although this mode of procedure for neutralizing the ester fraction proved effective, yet it was observed that the addition of water in excess of the amount needed to bring about this change

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[1] Schuette and Cowley, THIS JOURNAL, 53, 3485 (1931).

[2] The alcohols, with one exception, were Eastman products. They were distilled before use. *n*-Decanol was prepared for us in the laboratory of Professor Homer Adkins by B. H. Wojcik, who hydrogenated ethyl *n*-caprate over a copper-chromium-barium oxide catalyst [Folkers and Adkins, *ibid.*, 54, 1145 (1932)]. Their assistance is gratefully acknowledged.

in appearance of the carbonate is to be avoided, otherwise troublesome emulsions form. The neutral esters, without exception, were again fractionated under reduced pressure. Molecular refractions, computed by the formula of Lorenz and Lorentz, were used as a measure of the purity of the final product.

The properties of the esters so prepared are listed in Table I.

TABLE I

PHYSICAL PROPERTIES OF LEVULINIC ACID ESTERS

Alkyl	n^{20}	Specific gravity (20°/4°)	Molecular refraction (Lorenz–Lorentz) Obs.	Calcd.
n-Heptyl	1.4360	0.94332	59.365	59.391
n-Octyl	1.4380	.93635	63.754	63.994
n-Nonyl	1.4400	.93360	68.386	68.597
n-Decyl	1.4417	.92653	73.141	73.200

Specific Gravities.—Elsewhere[1] the suggestion was made that the specific gravities of the higher (liquid) members of this homologous series might be predicted with fair accuracy by means of the empirical formula $488.18d^2 - 1029.1d + 543.34 = c$, in which d and c represent specific gravity and number of carbon atoms in the alkyl radical, respectively. This was, however, not found to be the case with respect to all of the four new esters herein described for, with the exception of the *n*-heptyl derivative, each showed a deviation above the predicted value which is too large to be disregarded. Obviously the mathematical expression in question has a very limited use for predicting by extrapolation the specific gravities of the higher esters ($C_7 - C_{10}$). A better summation of the data at hand for the ten normal esters is given by the expression

$$d = 0.868686 + 0.772094/(c + 3.29699),$$

in which d and c have the same significance as in the preceding formula. The deviations will in no case exceed three-tenths of one per cent. when this formula is applied to these ten esters.

Vapor Pressures.—The isoteniscopic method of Smith and Menzies[3] was used for the determination of vapor pressures because it is more economical of material and more sensitive to the decomposition of these esters than is the dynamic method of Ramsay and Young.[4] Pressures were read from a closed manometer which had been checked against a standard barometer. Temperatures were determined by means of a two-junction, iron–constantan thermopile in connection with an accurate potentiometer and a reflecting galvanometer. The thermopile was calibrated against Bureau of Standards thermometers over the temperature range of the experiments. The isoteniscope bulb was suspended in a well-insulated air-bath provided with a carefully controlled electrical heating

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[3] Smith and Menzies, THIS JOURNAL, **32**, 1412 (1910).

[4] Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).

unit, a rapid stirrer and a small observation window. Maintaining the temperature constant to ±0.1° for a period of one-half minute was sufficient to allow for lag in the temperature-measuring device. Pressures are accurate to ±0.2 mm.; temperatures to ±0.2°.

Temperature–pressure relationships are expressed by means of the Kirchhoff[5] formula (Table II).

TABLE II

PRESSURE–TEMPERATURE RELATIONSHIPS OF LEVULINIC ACID ESTERS

Alkyl	Log P	B. p. (760 mm.), calcd. °C.
n-Heptyl	$19.3441-3.4634 \log T-3876.49/T$	283.5
n-Octyl	$16.9838-2.5904 \log T-3938.57/T$	291.1
n-Nonyl	$13.0149-1.2273 \log T-3855.21/T$	298.0
n-Decyl	$28.5652-6.0977 \log T-5120.54/T$	306.5

Discussion

That the esters decompose to form more volatile compounds upon heating was demonstrated by several observations. Vapor pressure data obtained for isobutyl levulinate by the static method[3] showed values in excellent agreement in the lower temperature range with those previously found by the dynamic method,[4] but definite deviations above those determined by the dynamic procedure were observed as the temperature was raised and the time of heating prolonged (Fig. 1). That this phenomenon may be indicative of decomposition has been noted in the case of *n*-valerolactone.[6] The beginning of the deviation is so definite that it recommends this method of dual determinations as a means of ascertaining the temperature at which decomposition begins. Data obtained for the new esters by the static method show at elevated temperatures similar high pressure values that cannot be made to conform to the Kirchhoff formula. Besides this, substantiation of this conclusion was found in the fact that a test run using *n*-octyl levulinate that had been once used for a vapor pressure determination gave high pressure values throughout the entire temperature range. Furthermore, it may not be without significance that all of the esters turned from colorless to yellow during the runs, the color being more intense at the surface exposed to the air.

The inconsistent pressure values (near atmospheric pressure) were disregarded in the formulation of the equations (Table II). The effect of decomposition is, therefore, to produce only a slight modification of the slope of the equation in the region of high pressure, which tends to make the calculated values for the boiling points slightly low and the values for the heats of vaporization and molar entropies slightly high.

Although the purified esters were kept in brown bottles protected from the light, they appeared to decompose partially upon standing. A fraction

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[5] Kirchhoff, *Ann. physik. Chem.* (*Poggendorf*), **103**, 185 (1858).

[6] Schuette and Thomas, THIS JOURNAL, **52**, 2028 (1930).

more volatile than the freshly prepared ester was obtained upon redistillation, the refractive index was lowered and the esters assumed a faint yellow color after a period of weeks. For this reason, freshly distilled material was used in the vapor pressure measurements.

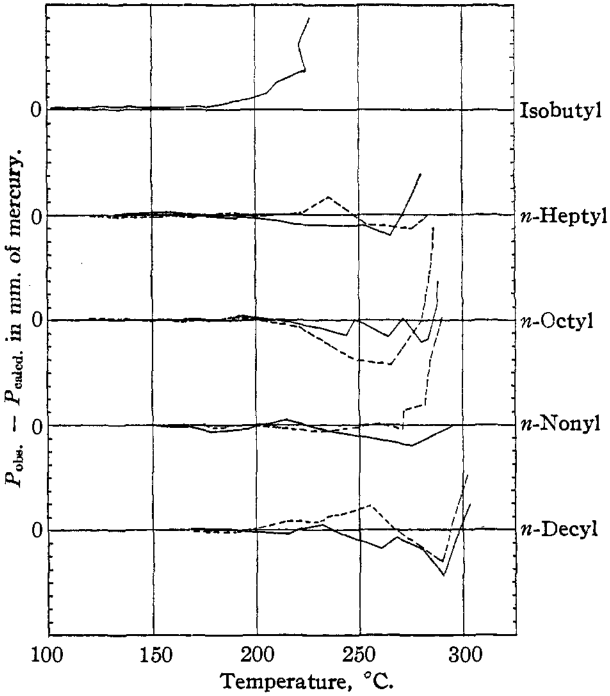

Fig. 1.—Deviation between observed and calculated vapor pressures of alkyl esters of levulinic acid. Ordinate graduations represent 10-mm. intervals; duplicate runs are indicated by unbroken and broken lines, respectively.

The excess of the molar entropies (Table III) over the average value of 27.3 given by Hildebrand[7] for normal liquids, is due in part to the result of decomposition though there is no apparent reason to suspect that the excess is not due partially to association of the liquids since all of the lower esters showed entropy values above the normal figure.

TABLE III

ENTROPIES OF VAPORIZATION OF THE ALKYL LEVULINATES

Alkyl	Temperature, °A.	Molar heat of vaporization (cal. mole)	Entropy of vaporization
n-Heptyl	496.2	14339.0	28.9
n-Octyl	507.2	15559.5	30.7
n-Nonyl	515.9	16341.8	31.7
n-Decyl	524.4	17210.0	32.8

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[7] Hildebrand, THIS JOURNAL, **37**, 970 (1915).

Summary

Four new esters of levulinic acid have been prepared and characterized by some of their physical properties. Evidence has been presented to show that these esters decompose at their boiling points near atmospheric pressure.

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The Photochemical Reduction of Ketones to Hydrols

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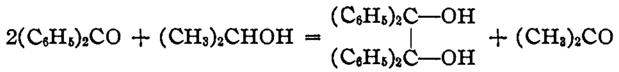
It has recently[1] been shown that a small amount of sodium alcoholate can effect the decomposition of a large amount of benzopinacol into a mixture of benzohydrol and benzophenone. It occurred to us that through this reaction it should be possible to obtain hydrols by photochemical reduction of ketones. From the classical work of Ciamician and Silber[2] it is known that if an alcoholic solution of benzophenone is exposed to sunlight, the benzophenone is reduced to benzopinacol at the expense of the alcohol, which is oxidized to aldehyde. Cohen[3] showed that a number of substituted ketones can be reduced to pinacols in the same manner and he found that a variety of primary and secondary alcohols can be used as reducing agents. It appeared that if a small amount of sodium alcoholate was present in the alcoholic solution of the ketone which was exposed to sunlight, a combination of the two reactions would take place: (1) reduction of the ketone to pinacol and (2) decomposition of the pinacol into hydrol and ketone. The ketone that is regenerated in the second reaction would go through the series of reactions until the hydrol was the sole product.

Actually, we found that if a small amount of sodium alcoholate is present in the alcoholic solution, the reduction proceeds exactly as expected; no pinacol is obtained; instead, the hydrol is formed in nearly quantitative yield. For the reaction we employed isopropyl alcohol in preference to ethyl alcohol because the reduction with this alcohol is more rapid and the oxidation product, acetone, is not affected by alkali so readily as is acetaldehyde. The reactions that take place are expressed in the following formulation



$$2(C_6H_5)_2CO + (CH_3)_2CHOH = \begin{array}{c}(C_6H_5)_2C{-}OH\\ |\\ (C_6H_5)_2C{-}OH\end{array} + (CH_3)_2CO \qquad (1)$$

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[1] Bachmann, THIS JOURNAL, **55**, 355 (1933).

[2] Ciamician and Silber, *Ber.*, **33**, 2911 (1900).

[3] Cohen, *Rec. trav. chim.*, **39**, 242 (1920).