

protect some of the chemical bonds in starch that would otherwise enter the measured reaction.

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RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
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A New Method for the Cleavage of Unsaturated Fatty Acids¹

BY CHI-YI HSING AND KOU-JEN CHANG

The methods for the cleavage of unsaturated fatty acids reported in the literature are either by energetic oxidations or by ozonization. On account of the side reactions, the degradation products are usually complex mixtures and the yields are very low.

Lead tetraacetate has been introduced by Criegee² as a reagent for the cleavage of glycols with excellent results. This oxidizing agent should be equally effective in oxidizing polyhydroxy fatty acids which in turn can be prepared easily from the corresponding unsaturated fatty acids by means of oxidation with alkaline potassium permanganate. It was found that 9,10-dihydroxyoctadecanoic acid (from oleic acid) was oxidized completely in twenty-four hours by lead tetraacetate in glacial acetic acid. As reaction products, pelargonic aldehyde and azelaic semialdehyde were isolated in the form of semicarbazones, each in a yield of about 85%. By using benzene as a solvent, 9,10,12-trihydroxyoctadecanoic acid (from ricinoleic acid, m. p. 111–112°) oxidized in four hours and about 90% of azelaic semi-aldehyde semicarbazone and a product melting at 112–113°, the character of which has not yet been determined, were obtained. A mixed melting point with starting material indicated it was different. The supposition is it may be β -hydroxypelargonic aldehyde semicarbazone or a related compound.

A more extensive study of this method for cleavage of unsaturated fatty acids of known and unknown structure will be reported later.

Experimental

In 10 cc. of glacial acetic acid which had been distilled over phosphorus pentoxide, was suspended 0.6740 g. of 9,10-dihydroxyoctadecanoic acid and to the mixture 0.95 g. of lead tetraacetate was added. This was shaken for twenty-four hours at room temperature. The solution was fil-

tered and heated in a water-bath at 45° for five minutes. It was then treated with 15 cc. of water and a concentrated aqueous solution of 0.5 g. of semicarbazide hydrochloride and 0.6 g. of sodium acetate was added. To the reaction mixture was now introduced a few drops of methanol and it was then vigorously shaken. After standing in an ice box for twenty hours, the semicarbazones separated as a white precipitate. The precipitate was filtered and shaken with cold dilute aqueous sodium hydroxide to dissolve the azelaic semialdehyde semicarbazone. Undissolved, impure pelargonic aldehyde semicarbazone was filtered and washed with water. The alkaline filtrate was acidified with 2% hydrochloric acid. The precipitated azelaic semialdehyde semicarbazone was filtered, washed and dried, yield 0.434 g. (90%). After purification by crystallization from ethanol it melted at 163–164° (Harries and Thieme³ reported 163°).

The alkali insoluble part consisted of lead chloride and pelargonic aldehyde semicarbazone. It was dissolved in methanol and the lead chloride was filtered. On evaporating the solution to a small volume, the semicarbazone separated as fine crystals melting at 99–100.5° (Bagard and Harries and Turk⁴ reported 100°). The yield was 0.348 g. (82%).

(3) C. Harries and C. Thieme, *Ann.*, **348**, 359 (1905).

(4) P. Bagard, *Bull. soc. chim.*, **4**, I, 346 (1907); C. Harries and H. O. Turk, *Ber.*, **40**, 2756 (1907).

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Dependence of Conductance on Field Strength

BY DARWIN J. MEAD AND RAYMOND M. FUOSS

We recently reported the field dependence of the conductance of tetrabutylammonium picrate in diphenyl ether at 50° [THIS JOURNAL, **61**, 2047 (1939)]. We are indebted to Dr. L. Tonks of this Laboratory for calling to our attention a correction which we neglected. The limit approached by the Wien coefficient at zero concentration now agrees with Onsager's theoretical value, when the correction factor of $8/3\pi$ is applied.

Our measurements were made in a bridge circuit, in which balance is indicated by zero current in a detector circuit fed through a low-pass filter. Our solutions were non-linear impedances, and the detector showed balance for only the fundamental frequency. According to theory, the specific conductance κ is given by

$$\kappa(t) = \kappa_0 + A V_m |\sin \omega t| \quad (1)$$

where κ_0 is the low voltage conductance, A is Onsager's coefficient and V_m is the peak voltage of the sinusoidal input at frequency f , with $\omega = 2\pi f$. The unit current then is

$$i(t) = \kappa_0 V_m \sin \omega t + A V_m^2 \sin \omega t |\sin \omega t| \quad (2)$$

(1) Presented at the 7th Anniversary Meeting of the Chinese Chemical Society, held at Kunming, China, August 29, 1939.

(2) R. Criegee, *Ber.*, **64**, 260 (1931); *Ann.*, **481**, 263 (1930); **507**, 159 (1933).

In order to find the fundamental in the non-linear term of (2), we simply expand it in a Fourier series

$$f(x) = \sin x | \sin x | = \sum a_n \sin nx$$

and take the first term, for which $a_1 = 8/3 \pi$. Then from the point of view of the bridge detector

$$i(t) = V_m \sin \omega t (\kappa_0 + 8AV_m/3\pi) \quad (3)$$

whence

$$\kappa = \kappa_0 + 8AV_m/3\pi \quad (4)$$

Our experimental result was

$$\kappa = \kappa_0 + B\bar{V} \quad (5)$$

where B is the experimental slope and $\bar{V} = 2V_m/\pi$ is the linear average voltage. Comparison of (4) and (5) gives

$$A = 3B/4 \quad (6)$$

which brings our experimental result into exact agreement with the theoretical value.

RESEARCH LABORATORY OF
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The Viscosity of Liquid Ammonia

By C. J. PLANK AND HERSCHEL HUNT

The viscosity of liquid ammonia is reported by Stakelbeck¹ to be 0.00218 g./cm. sec. at 20°, 0.00229 at 10°, 0.00238 at 0° and 0.00252 at -20°. He used the Lawaczev falling ball method. At -33.5° two values are reported, 0.002543² poise and 0.00260³ poise.

The viscosity of ammonia at room temperature is important. Since Stakelbeck's results have a small temperature coefficient, we re-determined the viscosity at 5, 15 and 25°. Our apparatus is shown in Fig. 1. The apparatus was carefully dried by heating it under reduced pressure. It was

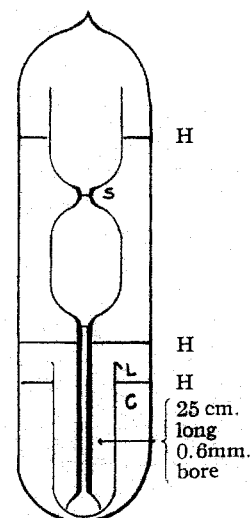


Fig. 1.—Viscometer.

calibrated with pure dry carbon disulfide and carbon tetrachloride. The following viscosities⁴ and densities of these compounds were used.

- (1) Stakelbeck, *Z. Kälte-Ind.*, **40**, 33-40 (1933).
- (2) Fitzgerald, *J. Phys. Chem.*, **16**, 621 (1912).
- (3) Eelsey, *THIS JOURNAL*, **42**, 2454 (1920).
- (4) Thorpe and Rodger, *Trans. Roy. Soc. (London)*, (**A**)**185**, 397 (1895).

Temp.	Carbon disulfide Density	Carbon disulfide Viscosity	Carbon tetrachloride Density	Carbon tetrachloride Viscosity
5°	1.2856	0.004125	1.6230	0.01233
15°	1.2750	.003805	1.6037	.010476
25°	1.2554	.003565	1.5843	.009027

The constants, C and C' , of the equation

$$\eta = C\rho t - C'\rho/t$$

were determined at each temperature. The ammonia was dried over sodium and distilled under reduced pressure into the apparatus. After the outside jacket was sealed the apparatus could be rotated in order to fill the viscometer with the liquid. The supports, H's, held the viscometer perfectly vertical and rigid within the jacket when the outside jacket was placed in a vertical position.

The determinations were made in an air thermostat whose temperature was regulated to 0.05°. The time was measured with an accurately calibrated stop watch. Since the time of flow was in the neighborhood of four to eight minutes for the calibration and almost four minutes for the ammonia, the error in the measurement of time was not over 0.02%.

The apparatus was designed as shown because a closed system was necessary, and by having container C full of liquid when the meniscus passes S, a constant head was ensured. A fine lip, L, on C ensured a delivery of the liquids at the same level, so that a change in surface tension of the liquids did not interfere. The small head also increased the time of flow. It is difficult to fill the apparatus with cold ammonia by distillation and get the desired hydrostatic head when the liquid becomes warm. Two viscometers were used and the results are in excellent agreement. The viscosities and densities at the three temperatures are:

Temp., °C.	Density g./cc.	Viscometer number 1	Viscometer number 2	Viscosity of NH ₃ (av., g./cm. sec.)
5°	0.63197	0.001628	0.001607	0.001618
15°	.61821	.001468	.001446	.001457
25°	.60427	.001350	.001350	.001350

The densities were determined by the pycnometer method. These data, if we can judge by the long extrapolation, are in good agreement with the low temperature values in the literature. Stakelbeck's results would indicate that the temperature coefficient of viscosity for ammonia is much smaller than the coefficient for any other known liquid. His results agree with ours if we multiply