

Preparation and Properties of Tridecanoic Acid Containing C¹⁴ in the Carboxyl Group

Edward Hines and Andrew Gemant

Research Department, The Detroit Edison Company

An organic electrolyte containing a radioactive isotope was required in order to carry out studies of mobilities and molecular sizes of ion-forming compounds in dielectric liquid (2), particularly insulating oils. A previous paper (3) indicated that any aliphatic acid having a molecular weight equal to or greater than that of propionic acid is suitable for obtaining the electrical conductivity necessary. The further requirement of low vapor pressure, to minimize contamination of the laboratory atmosphere with radioactive vapor, limited the range to acids of molecular weight greater than that of capric acid. Consideration of these requirements of the compound, the means of preparing it, and the available starting materials led to the selection of tridecanoic acid containing C¹⁴ in the carboxyl group.

The tridecanoic acid was prepared from lauryl bromide and carbon dioxide by the Grignard reaction, the carbon dioxide being obtained by acidification of barium carbonate containing C¹⁴. Unlike the usual carbonation of Grignard reagents, this reaction necessitated the use of an excess of Grignard reagent rather than an excess of carbon dioxide, because of the expense of the radioactive isotope used. Since the use of excess Grignard reagent favors the formation of secondary products, such as ketones and alcohols (4), the carbonation and subsequent hydrolysis were carried out as rapidly as possible.

Purification from secondary products was carried out by saponification and reprecipitation of the acid.

The purified acid crystallized as white plates, having a melting point of 39.5° to 41.5° C. This compares with 40.5° C found by Krafft (5), 40° C by Blau (1), and 42.5° C by Le Sueur (6). The refractive index was found to be 1.427 n_D at 60° C, which is in close agreement with the value of 1.4249 n_D at 70° C obtained by Waterman and Bertram (9). Values of 72.8% carbon and 12.4% hydrogen were obtained by ultimate analysis. These values approximate the theoretical values of 72.8% carbon and 12.2% hydrogen.

The apparatus used for the carbonization of the Grignard reagent consisted of a generating flask, drying tube, and reaction flask, interconnected in the order named. The generating flask contained barium carbonate (0.024 mole) having 2 mc of C¹⁴. The radioactive barium carbonate was purchased from the United States Atomic Energy Commission. The drying tube contained anhydrous calcium chloride and the reaction flask contained the Grignard reagent prepared from lauryl bromide. This system was evacuated prior to the carbonation so that a partial vacuum would exist in the apparatus throughout the synthesis, thus preventing the leakage of radioactive vapors into the laboratory atmosphere.

Carbon dioxide was generated from the barium carbonate at such a rate as to keep gas pressure in the sys-

tem constant at slightly below atmospheric pressure. It was passed through the drying tube into the reaction flask as it was generated and, upon completion of the acidification of the barium carbonate, the carbon dioxide remaining in the system was flushed into the reaction flask with small charges of dry nitrogen until the system had reached atmospheric pressure. The contents of the reaction flask were then hydrolyzed in the usual manner on crushed ice.

The entire reaction from the beginning of the carbonation to the completion of the hydrolysis was carried out within 5 min.

One gram of the product was melted and spread over an area of 20 cm², then permitted to crystallize, yielding a layer of about 0.05 cm in thickness. An open area of 4.7 cm² was screened out for a count test with a Geiger-Müller counter having a mica window 2.54 cm in diameter and 2.8 mg/cm² in thickness. The distance between the sample and the mica window was 9.1 cm. The net counts obtained were 28/sec.

In order to compare this figure with the theoretically expected count, the latter was computed in the following manner. The upward activity I of a layer of thickness ρ g/cm², an area of A cm², and containing σ mc/g, corresponds to

$$I = \frac{A\sigma}{2\mu} (1 - e^{-\mu\rho})$$

where μ = absorption coefficient in cm²/g of the radiation in question (7). If ρ equals or is larger than the range of the betas, the exponential term becomes zero and the bracket is unity. This was the case in this test, since the range of 0.14-Mev betas is 20 mg/cm².

From the chemical synthesis, 2 mc of C¹⁴ should be present in about 0.024 mole of tridecanoic acid, i.e., in 5.2 g of the acid. In other words, $\sigma = 0.39$ mc/g. With $\mu = 270$ cm²/g for the electrons of radioactive carbon (8), we have $I = 0.0034$ mc, or, converted into counts, 1.25×10^5 counts per sec.

From the geometry of the arrangement, the spatial angle (in terms of 2π) that the mica window represents in $1 - \cos \tan^{-1} (1.27/9.1) = 0.0097$. Hence the counts corresponding to this spatial angle are 1200 per sec.

The mass of air between the sample and the counter is 10.9 mg/cm², to which must be added the mass of the mica window, giving 13.7 mg/cm². The relative intensity of betas escaping absorption is then $\exp(-270 \times 13.7 \times 10^{-3}) = 0.024$. The number of betas that should reach the counter is then 29 per sec. This is in good agreement with the experimentally obtained value of 28 per sec.

References

1. BLAU, J. *Monatsh.*, 1905, **26**, 107.
2. GEMANT, A. *J. appl. Phys.*, 1948, **19**, 1160.
3. ———. *J. electrochem. Soc.*, 1948, **94**, 160.
4. GILMAN, H. *Organic chemistry*. New York: John Wiley, 1945, Vol. I, p. 506.
5. KRAFFT, F. *Ber.*, 1879, **12**, 1669.
6. LE SUEUR, H. R. *J. chem. Soc.*, 1905, **87**, 1888.
7. LIBBY, W. F. *Ind. eng. Chem.*, 1947, **19**, 2.
8. NORRIS, D. and INGRAM, M. G. *Phys. Rev.*, 1948, **73**, 350.
9. WATERMAN, H. I. and BERTRAM, S. H. *Rec. trav. chim.*, 1927, **46**, 699.