[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE OAK RIDGE NATIONAL LABORATORY]

# The Reaction of 9-Formylfluorene-10-C$^{14}$ with Formaldehyde[1]

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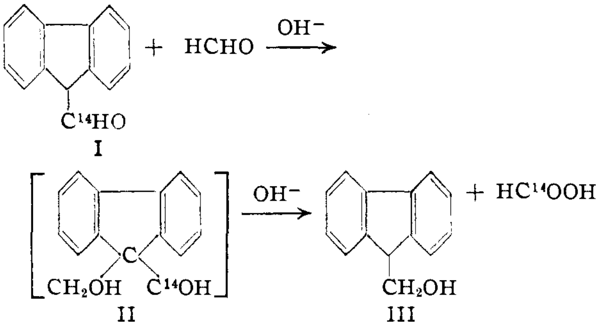
The reaction of 9-formylfluorene-10-C$^{14}$ with aqueous formaldehyde has been found to produce non-radioactive 9-fluorenemethanol. The radioactivity was accounted for quantitatively as formate ion. These facts are explained by a mechanism which includes as an intermediate the aldol formation of an unstable tertiary aldehyde.

## Introduction

The action of excess aqueous basic formaldehyde solution upon 9-formylfluorene has been found to give 9-fluorenemethanol.[2] The usual action of this reagent on aldehydes with one alpha hydrogen gives $\beta,\beta$-disubstituted trimethylene glycols.[3]

It has now been discovered that the action of excess aqueous basic formaldehyde solution upon 9-formylfluorene-10-C$^{14}$ (I) gives 9-fluorenemethanol which is non-radioactive. Substantially all of the C$^{14}$-activity appears as formate ion. Unreacted formaldehyde is non-radioactive ruling out any exchange between formylfluorene and formaldehyde, or between formate and formaldehyde. Thus, the mechanism shown below, which was suggested by Brown and Bluestein,[2] has been supported. The instability to alkali of the tertiary aldehyde (II) is paralleled by the instability to alkali of other highly negatively substituted tertiary aldehydes such as chloral, triphenylacetaldehyde and acetylenic aldehydes.[4]



Since it is probable that the factor which decides whether a tertiary aldehyde such as II will cleave or undergo a crossed Cannizzaro reaction to give a disubstituted trimethylene glycol is the stability of the ionic intermediate which would result from loss of the aldehyde group, the reactions of formaldehyde with other C$^{14}$-labeled aldehydes are now under study in this Laboratory.

## Experimental[5]

**Formic Acid-C$^{14}$, Ethyl Ester.**—This was prepared by the general procedure of Ropp.[6] The sodium formate solution from a 1 mc. ampoule was rinsed into a flask containing 682 mg. of non-radioactive sodium formate. This solution was distilled to dryness under high vacuum, and the dry residue was heated to 170–210° for one-half hour with 5 ml. of triethyl phosphate. The product was then distilled at high vacuum, and redistilled about 10 mm. pressure into a graduated tube. The volume of distillate was 0.80–0.82 ml. and had a vapor pressure at 0° of 77.5 mm. This ester was distilled under high vacuum into a flask containing 7.0076 g. of non-radioactive ethyl formate. The gain in weight was 770 mg. (a 100% yield of ethyl formate from sodium formate). By the procedure described below, a portion of this ester was converted to formylfluorene benzoate, which was then assayed for C$^{14}$. The assay showed an activity of 9.72 $\mu$c./mmole. This corresponds to a total activity of 1.02 mc., or a radiochemical yield of 100% from the ampoule of sodium formate-C$^{14}$.

**9-Formylfluorene-10-C$^{14}$ (I).**—This was prepared by the procedure of Wislicenus and Waldmuller[7] from 2.0 g. of purified fluorene (m.p. 12.0 mmole), 1.0 g. of ethyl formate-C$^{14}$ (13.5 mmole, activity of 9.72 $\mu$c./mmole), and the potassium ethoxide from 0.5 g. of potassium (12.8 mmole). The neutral solid from the hydrolyzed reaction solution weighed 0.54 g. (27%) and was shown to be fluorene by mixture melting point. The aqueous layer of the hydrolyzed reaction solution (18 ml. in volume) was light yellow brown. It was warmed on the steam-bath to remove ether. A 4-ml. portion was diluted with an equal volume of 20% sodium hydroxide and the solution was shaken with benzoyl chloride. The white clumpy benzoate which separated was crystallized from dilute alcohol and then melted at 157–158° (lit.[7] 158–159°). This material assayed for 9.72 $\mu$c. of C$^{14}$/mmole, and was used as mentioned above to determine the specific activity of the ethyl formate preparation.

**9-Fluorenemethanol (III).**—The remainder of the aqueous fraction of the hydrolyzed reaction product from above was stirred vigorously while 10 ml. of 10% formalin solution was gradually added. The yellow solution almost immediately became colorless and an oil deposited which quickly solidified. This solid was filtered. After drying it weighed 1.43 g. (100% yield from reacted fluorene). It was crystallized twice from hexane to give large colorless needles melting at 99–100°. Upon assay for C$^{14}$ content, the carbinol showed only background activity. This reaction was repeated several times with the same result.

In another run, employing exactly one-quarter of the above quantities, the aqueous filtrate from the fluorenemethanol precipitate was evaporated almost to dryness, after 1.057 g. of non-radioactive sodium formate had been added. The residue was made slightly acid with hydrochloric acid and diluted to 12 ml. To this was added 10 ml. of 20% S-benzylthiuronium chloride solution. On standing, large crystals of S-benzylthiuronium formate deposited. These melted at 148–149°, and assayed for 1.385 $\mu$c. of C$^{14}$/mmole. This corresponds to a total of 22 $\mu$c. of C$^{14}$ activity as formate ion, compared with an estimated total initial activity as formylfluorene of 23 $\mu$c. (based on 75% yield from fluorene).

In another run, this same aqueous fraction was treated with methone. The precipitated dimedon-formaldehyde derivative was crystallized from ethanol. Upon assay for C$^{14}$ content, it showed only background activity.

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(1) This document is based upon work performed for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) Brown and Bluestein, THIS JOURNAL, **65**, 1082 (1943).

(3) Adams, "Organic Reactions," Vol. II, John Wiley and Sons, New York, N. Y., 1949, p. 100.

(4) *Ibid.*, p. 99.

(5) All melting points were taken on a Fisher–Johns block and are uncorrected. C-14 assays were accomplished by a wet combustion of the compounds, and ionization chamber counting of the carbon dioxide on a vibrating reed electrometer.

(6) G. A. Ropp, THIS JOURNAL, **72**, 2299 (1950).

(7) W. Wislicenus and M. Waldmuller, *Ber.*, **42**, 786 (1909).