corresponding times as ordinates. The cell C_a is exposed (using both positions) until the quantity of oxalic acid decomposed is measurable with the degree of precision desired. The area under the curve is divided into strips by ordinates at those times which mark the various stages of the experiments. The area of any strip is proportional to total quanta emerging from either exit slit during the corresponding time interval. Corrections for reflection and transmission are made as stated above. Let A_g be the area of the strip corresponding to a given exposure of C_g, and $(A_a + A'_a)$ the sum of the areas for the two exposures of C_a. Also let $\Sigma(h\nu)_g$ and $\Sigma(h\nu)_a$ be corrected total quanta absorbed, and Δm_g, Δm_a the moles transformed during the same time intervals. Then $\phi_g = \phi_a \Delta m_g \Sigma(h\nu)_a / \Delta m_a \Sigma(h\nu)_g = \phi_a \Delta m_g (A_a + A'_a) / \Delta m_a A_g$.

If the apparatus is carefully handled, the ratio $(A_a + A'_a)/\Delta m_a$ remains constant and reproducible within experimental error, and need not be rechecked for each refilling of the gas cell.

Summary

An apparatus and a method are described whereby the quantum yield of a photochemical gas reaction over any time interval during its progress may be stated in terms of the quantum yield of uranyl oxalate in monochromatic light of the same wave length with a probable error of five per cent.

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A NEW METHOD FOR THE DETERMINATION OF PROPIONIC ACID

BY JAMES B. MCNAIR

There is a need for a suitable method for the quantitative estimation of propionic acid in the presence of formic and acetic acids. This becomes of special importance in connection with the analysis of acids produced by fungi. The fact that oxalic acid is produced by the following method from propionic acid but is not formed from formic and acetic acids under the same circumstances serves as a basis for a new method for the determination of propionic acid.

Method.—To every 5.94 cc. of 0.1 N propionic acid, 1.5 g. of anhydrous sodium carbonate, 17.5 cc. of 3.12% potassium permanganate, and 27 cc. of distilled water are added in a 250-cc. Pyrex Erlenmeyer flask. This flask is capped by a small glass beaker and the entire Erlenmeyer covered by a large glass beaker and placed on a steam-bath for four hours. After that time the Erlenmeyer is removed from the steam-bath and 5 cc. of 95% alcohol added to eliminate the excess potassium permanganate. The manganese dioxide is separated by filtering the mixture through an alundum crucible under suction. The alundum crucible is placed in a

funnel, the stem of which passes through the neck of a bell jar into a beaker. The crucible is washed five times with distilled water before and after filtering the manganese dioxide. The filtrate is now acidified with glacial acetic acid and 3 g. of calcium acetate added and let steam overnight. The precipitate (calcium oxalate) is collected on an alundum crucible by filtration and washed with four fillings of distilled water. The crucible and contents are now placed in a 250-cc. beaker. Ten cc. of concentrated sulfuric acid is added just before the final titration with 0.04 N potassium permanganate. During the titration the acid liquid is kept at a temperature of 65 to 70° and the titration with potassium permanganate continued until the rose tint remains permanent for two minutes.

Two check experiments required for each 5.94 cc. of 0.1 N propionic acid 18.60 and 18.60 cc., an equivalent of 7.44 of 0.1 N potassium permanganate.

It was found that with the above amounts of material the formation of oxalic acid was not complete with less than three hours of heating on the steam-bath. When experiments were first begun with this method the excess potassium permanganate was oxidized with hydrogen peroxide formed by the addition of sodium peroxide. All glassware used in the experiment had been cleaned with dichromate sulfuric acid cleaning mixture.

Summary

A new method has been described for the determination of propionic acid. In this method propionic acid is oxidized to oxalic acid. Such a method is especially valuable in the determination of propionic acid in the presence of formic and acetic acids.

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THE ELECTRON AFFINITY OF FREE RADICALS. IV. COMPOUNDS NOT AROMATIC HYDROCARBONS

BY H. E. BENT, M. DORFMAN AND W. F. BRUCE

In the three previous papers of this series[1] values for the free energy change of the reaction of addition of sodium to eight organic free radicals have been reported and by combination with appropriate equations the electron affinities in the gaseous state calculated. These free radicals contained only phenyl, biphenyl or naphthyl groups attached to the trivalent carbon atom. The values of ΔF for the reaction[2]

[1] H. E. Bent THIS JOURNAL. **52**, 1498 (1930); **53**, 1786 (1931); Bent and Dorfman. *ibid.*, **54**, 1393 (1932).

[2] The standard state is the metal in the case of the sodium and for the other species the activity is taken as equal to the mol fraction.