tive, but other salts apparently equally as well. This seemed so striking that we immediately endeavored to verify this observation in a somewhat more exact manner.

A small tube (2.4 cm. in diameter) was rotated (3 r. p. m.) on its long axis inside a split type laboratory combustion furnace. A short (4 cm.) length of the tube, in the center of the furnace, and having a negligible temperature gradient, was coated completely with the salt in question. Thus the concentration of the salt was assumed to be constant at the carbon–salt interface. The temperature of the furnace was then increased to and maintained at a predetermined convenient value (±3°). Carbon film deposition, mirror reflected observation, and air admittance were made through a narrow longitudinal slot (2 cm. wide) in the under portion of the surrounding furnace. The apparatus was entirely enclosed in a small glass-fronted cabinet to protect it from drafts.

Carbon deposition was carried out by means of a wide flame of enriched natural gas from a Pyrex glass burner which moved mechanically along the slot in the furnace at a uniform rate (0.02 cm./sec.). The flame deposited the carbon film uniformly, as evidenced by the manner in which it disappeared on oxidation, and at a rate of 3.5 micromoles/sec., reproducible within 10%.

The lengths of time required for the disappearance of the carbon film from the 4 cm. sector were determined when deposited on bare glass as well as on the following C. P. salts: lithium, sodium, potassium, calcium, strontium and barium chlorides, calcium and barium hydroxides, sodium and potassium sulfates.

At 575° the carbon burned off the bare glass in about 180 sec. This was cut down by all of the salts to between 20 and 30 sec., as far as could be discerned by the method of observation. At 550° the oxidation of the carbon from the bare surface required 280 sec. It was reduced by the presence of the salts to 130–150 sec. At 515°, the oxidation from the bare surface required 630 sec. This was cut down by the barium and strontium salts to about 300, by the calcium salts and sodium chloride to about 230, and by the potassium and lithium chlorides, and sodium and potassium sulfates to about 170 sec. The values given are the averages of two or more observations usually agreeing within 10% or less. This agreement evidences a fair reproducibility of oxidizable surface area.

The most ready explanation of the effect of salts in the oxidation of carbon is that offered by Taylor and Neville.[3] They pointed out that the probable function of salts in the reaction of steam on carbon is in hastening the decomposition of the C_xO_y surface complex. With this barrier removed, a carbon surface is more readily attacked by oxidizing gases.

[3] H. S. Taylor and H. A. Neville, THIS JOURNAL, **43**, 2055 (1921).

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The Isolation and Identification of a Paraffin Hydrocarbon from Urine of Pregnancy

BY WILLIAM FORRIS HART AND M. ALLEN NORTHUP

Marrian[1] has mentioned that a paraffin hydrocarbon which is physiologically inactive, occurs in urine of pregnancy. Schwenk[2] also states that he has encountered a physiologically inactive hydrocarbon in urine of pregnancy.

We have isolated and identified one hydrocarbon, heptacosane, from urine of pregnancy, and have evidence of the presence of another, pentacosane, in the same material.

Experimental.—Twelve liters of urine were aged for several months and acidified to Congo red with concentrated hydrochloric acid, the acidified urine was then treated with 28 g. of fuller's earth per liter, agitated thoroughly, and allowed to stand overnight. The fuller's earth was then filtered off, and a second absorption on 14 g. per liter was applied. The combined fuller's earth fractions were air dried and extracted seven times with convenient volumes of low boiling petroleum ether (below 70°). The combined petroleum ether residue was taken up in 50 cc. of ethyl acetate. This solution, on chilling, deposited 1.4 g. of white plate-like crystals. It was found on recrystallizing from methanol that this material could be separated into two fractions, one soluble, and the other insoluble, in warm methanol.

The fraction insoluble in warm methanol was recrystallized repeatedly from ethyl acetate. The final melting point was 58–59° (uncorrected). Analysis gave: C, 85.83 and 84.56, H, 14.62 and 14.62; molecular weight (micro Rast), 391, 391. Calcd. for heptacosane ($C_{27}H_{56}$): C, 85.16,

[1] Marrian, *Physiol. Rev.*, **13**, 185 (1933).

[2] E. Schwenk, private communication.

H, 14.83; molecular weight, 380; melting point, 59°.[3]

The fraction soluble in warm methanol was recrystallized repeatedly from ethyl acetate. The final melting point was 52–54° (uncorrected). Analysis gave: C, 85.07; H, 15.08%. Calcd. for pentacosane ($C_{25}H_{52}$): C, 85.37; H, 14.63; melting point, 54°.[3]

It is not certain whether this fraction consists of a pure hydrocarbon, or a mixture of two or more hydrocarbons. On crystallizing from ethyl acetate on a microscope slide it has the form of homogeneous hexagonal plates.

Besides the solubilities mentioned above, these fractions are very soluble in chloroform and benzene, soluble in hot and insoluble in cold acetone and ethanol, and insoluble in water and alkali.

They contain no nitrogen or phosphorus, have no acid or saponification number, do not reduce Fehling's solution, and do not absorb bromine from chloroform solution. They have been found to have no oestrogenic activity.

The procedure outlined above was applied to eight liters of non-pregnant female urine which had been aged for two weeks. From the petroleum ether was obtained 3.8 mg. of an impure waxy substance from which it was not possible to isolate any crystalline material melting below 120°.

The same procedure was also applied to two samples of male urine of eight liters each. One of these was a year old; the other had been aged two weeks. Like the non-pregnant female urine each yielded a few milligrams of impure waxy substance from which no crystalline material melting below 120° could be isolated. If these hydrocarbons occur in non-pregnant female, and male, urine they must do so in an amount far less than in urine of pregnancy. The physiological source of these hydrocarbons during pregnancy raises many interesting speculations.

The authors regret that factors beyond their control have prevented an extension of this investigation. They wish to thank Dr. F. R. Eldred, Director of Research, of Reed and Carnrick, for his kind permission to publish this work, and Dr. J. B. Niederl of Washington Square College, New York University, for the micro analyses and molecular weight determinations.

[3] Hildebrand and Wachter, This Journal, **51**, 2487 (1929).

A Contribution from the
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Preparation of Alpha-Naphthoic Acid

By D. J. Loder[1] and F. C. Whitmore

During some work which demanded the preparation of a considerable amount of pure alpha-naphthoic acid, all of the regular methods of preparing this substance were tried with only mediocre success. At the same time some studies were being carried out on the preparation of tertiary alcohols by the action of the Grignard reagent with diethyl carbonate and it had been observed that when the Grignard reagent was "sterically hindered" the reaction could be stopped at the ketone stage or even at the ester stage. Consequently, alpha-naphthylmagnesium bromide (5 moles in 2.5 liters of absolute ether) was added slowly to a solution of ethyl carbonate (7.5 moles in 500 cc. of dry ether). Treatment of the mixture with a slight excess of 30% sulfuric acid, separation of the ether layer and isolation in the usual way gave a 70% yield of redistilled ethyl alpha-naphthoate boiling at 143–144.5° at 3 mm. Hydrolysis of the ester gave over a 90% yield of pure alpha-naphthoic acid.

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The Mechanism of the Addition of Halogens to Ethylenic Linkages

By Richard A. Ogg, Jr.

The addition in solution of halogens to an ethylenic linkage is assumed by Ingold[1] to proceed through the formation of an intermediate positive carbonium ion, as $\mathrm{RCHBr{-}C^{+}HR}$, which subsequently adds a halide ion. Experiment indicates positive carbonium ions to be configuratively unstable,[2,3] and hence this mechanism would lead one to expect identical products (*i. e.*, a mixture of meso and *dl* dihalides) from *cis–trans* isomers, in contradiction to experimental fact.

Carothers[4] has proposed that addition reactions of ethylenic linkages are initiated by an internal ionization of the double bond, followed by addition of the reagent molecule at the positive end,

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[1] C. K. Ingold, *Chem. Reviews*, **15**, 225 (1934).

[2] E. S. Wallis and F. H. Adams, This Journal, **55**, 3838 (1933).

[3] E. Bergmann and M. Polanyi, *Naturwissenschaften*, **21**, 378 (1933).

[4] W. H. Carothers, This Journal, **46**, 2227 (1924).