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.

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[3] Hildebrand and Wachter, THIS JOURNAL, **51**, 2487 (1929).

A CONTRIBUTION FROM THE
LABORATORIES OF REED AND CARNRICK
JERSEY CITY, N. J.
RECEIVED OCTOBER 25, 1935

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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STATE COLLEGE, PENNSYLVANIA
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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 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).

and subsequent rearrangement to the stable addition product. Such an internal ionization of double linkages, in view of the rapid racemization of positive carbonium ions, would cause a rapid *cis–trans* isomerization of ethylene derivatives even in the absence of reagents. Hence this mechanism is open to the same objection as that of Ingold, *i. e.*, in leading to identical addition products from *cis–trans* isomers. Both mechanisms infer the addition reactions in question to be uncatalyzed.

The following mechanism is suggested as more plausible. Using bromine, for example, the consecutive reactions are

$$(1)\quad Br^- + RCH{=}CHR \longrightarrow RCHBr{-}C^-HR$$

$$(2)\quad RCHBr{-}C^-HR + Br{-}Br \longrightarrow RCHBr{-}CBrHR + Br^-$$

That is, the addition is catalyzed by halide ion, and the intermediate is a carbanion. Carbanions have been shown[2] to have stable configurations, and hence stereochemically different products should result from *cis–trans* isomers. Further, explanation is afforded of the generally observed *trans* addition of halogens to ethylenic linkages. Reaction (1) is to be regarded as a substitution reaction of the halide ion with one of the electron pair bonds of the ethylenic linkage, and hence as attended by *optical inversion* of the intermediate carbon atom.[5] The carbanion thus has a *trans* configuration, and since no configuration change attends reaction (2), the final addition product should be *trans*.

Experimental evidence for the proposed mechanism is found in a number of cases in which addition or removal of halogens from an ethylenic linkage is catalyzed by halide ions. Thus Slator[6] found the decomposition of ethylene diiodide to be catalyzed by iodide ions in alcoholic solution. Obviously the addition of iodine to ethylene must be similarly catalyzed. Reaction of a 1,2-dibromo compound with iodide ions to yield the corresponding unsaturated compound is a well-known typical reaction. Halogen addition to simple ethylenic hydrocarbons in solution is ordinarily exceedingly rapid. However, the marked slowness of the addition of bromine to ethylene in rigorously purified and dried solvents[7] indicates the ordinary reaction to be catalyzed by impurities, of which halide ions appear most likely. The otherwise immeasurably slow addition of bromine to maleic and fumaric esters was found by Hanson and Williams[8] to be catalyzed by a trace of hydrogen bromide. Finally, the author has observed, using glacial acetic acid as a solvent, that the normally slow addition of bromine to maleic and fumaric acids, stilbene, cinnamic acid and tetrachloroethylene is markedly catalyzed by dissolved lithium and potassium bromides.

A very similar mechanism to the above probably obtains for addition of hydrogen halides to ethylenic linkages, step (2) being replaced by addition of a hydrogen ion to the carbanion. *Trans* addition should also occur in this case. Likewise the addition of halogens and hydrogen halides to acetylenic linkages should proceed in analogous fashion, giving *trans* addition products, as is actually observed.

It is to be emphasized that the above mechanism applies to reactions in solution, and in the dark. Gas phase addition of halogens to double bonds cannot of course be caused by ionic catalysis, and it is significant that no homogeneous reaction of gaseous ethylene with bromine or chlorine[9,10] is observed at low temperatures. In the photochemical reaction the chains are carried by free halogen atoms and the radicals RCHBr—CHR. The rapid racemization of the latter, followed by loss of halogen atoms, explains the well-known halogen-sensitized *cis–trans* isomerization of ethylene derivatives. Likewise, the photochemical reaction is to be expected to lead to a mixture of *cis* and *trans* addition products.

Cases in which marked *cis* addition of halogens occurs practically all involve the *ions* of maleic and fumaric acids.[11] Due to the Coulomb repulsion between the negative charges of the halide ion and of the acid ions, the above mechanism could hardly be expected to obtain. It is much more probable that intermediate lactone formation occurs, in which case the *cis* addition is readily explicable.

The recent communication of Anantakrishnan and Ingold[12] substantiates the above suggestion that halogen addition to ethylenic hydrocarbons is catalyzed by halide ions.

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[5] N. Meer and M. Polanyi, *Z. physik. Chem.*, **19B**, 164 (1932); A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[6] A. Slator, *J. Chem. Soc.*, **85**, 1697 (1904).

[7] H. S. Davis, THIS JOURNAL, **50**, 2769 (1928).

[8] N. W. Hanson and D. M. Williams, *J. Chem. Soc.*, 1059 (1930).

[9] Stewart and Edlund, THIS JOURNAL, **45**, 1014 (1923).

[10] R. G. W. Norrish, *J. Chem. Soc.*, **123**, 3006 (1923).

[11] Terry and Eichelberger, THIS JOURNAL, **47**, 1067 (1925).

[12] S. V. Anantakrishnan and C. K. Ingold, *J. Chem. Soc.*, 984 (1935).