NOTES

Cyclopentanes and Petroleum Origin

By Benjamin T. Brooks

Cyclopentanes and cyclopentenes are not found in nature in plants or essential oils and five carbon ring structures are only very rarely found in complex substances such as pyrethrin, jasmone as a minor component in oil of peppermint and in the perfume oil of jasmine, chaulmoogric acid and combined with other ring structures as in a few of the triterpenes and isoprenic steroids. Cyclopentanes are found in the gasoline fractions of all types of petroleums, and in many cases, in substantial proportions. The careful analyses of seven petroleums made by Rossini[1] and his co-workers show the following percentages of cyclopentanes in the gasoline fraction distilling in the range 40–180°.

Crude source	Total cyclopentanes, per cent. by volume
Ponca, Okla.	8.86
East Texas	11.03
Bradford, Pa.	5.49
Greendale, Mich.	3.32
Winkler, Texas	5.46
Midway, Calif.	13.61
Conroe, Texas	5.66

In view of the extreme rarity of the five carbon ring structure in nature, the presence of cyclopentanes in petroleums is certainly not due to degradation of any natural products containing such structures. It is suggested that the cyclopentanes in petroleums have been formed by rearrangement of cyclohexanes. Such rearrangements have been observed experimentally at temperatures as low as 25° by the action of moist aluminum chloride.[2] It is believed that the occurrence of cyclopentanes in petroleums gives support to the theory that active surface minerals act catalytically in forming the wide diversity of hydrocarbons found in petroleums. Other evidence for this has been more fully presented in other papers.[3]

There is no constant relation between the per cent. of cyclohexane and methylcyclopentane and no relation between the ratios of these hydrocarbons and present bottom hole temperatures. The ratios of these two hydrocarbons do not correspond in the case of the gasolines noted, to the calculated thermal equilibrium compositions for any particular small temperature range and the high ratio of methylcyclopentane to cyclohexane found in some cases, 4.03% methylcyclopentane to 2.04% cyclohexane in East Texas gasoline, is far out of line with the equilibrium compositions found experimentally (in the presence of aluminum chloride). At 77.4° the experimental equilibrium mixture contained 25.6% methylcyclopentane and lower percentages at lower temperatures. The lowest ratio of methylcyclopentane to cyclohexane in any of these gasolines was 2.97 to 4.34 in the Conroe, Texas, gasoline, or 39% of the sum of these two hydrocarbons. The composition of gasolines is full of similar inconsistencies when reference is made to calculated thermal equilibrium compositions. One such calculation led to a temperature of petroleum formation within the range of commercial cracking processes, a condition which is clearly precluded by the time element as well as many of the facts as to chemical composition of crude petroleum.

405 Lexington Avenue
New York 17, N. Y.
Received September 30, 1949

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(2) A. L. Glasebrook and W. G. Lovell, This Journal, **61**, 1717 (1939).

(3) B. T. Brooks, *Am. Assn. Petr. Geol.*, **32**, 2269 (1948); **33**, Sept. (1949).

Enzymatic Hydrolysis of Steroid Hormone Esters by Blood Serum[1]

By Fritz Bischoff, Robert E. Katherman, John J. Moran and Yee Sing Yee

The solubilities of testosterone, progesterone and estradiol in mammalian blood serum are accounted for by the solubilities of these substances in solutions of the serum constituents.[2,3] Testosterone propionate and estradiol benzoate,[4] are much less soluble in solutions of serum constituents than the corresponding free steroids, but the solubilities of these esters in serum on equilibration approach the solubilities of the free parent steroids. These results can be explained only by postulating the existence of a serum steroid hormone esterase.

Proof for this enzymatic hydrolysis by rabbit, bovine and human serum has been established using the Folin-Ciocalteu phenol reaction with estradiol benzoate as substrate. The benzoate ester gives no color with the phenol reagent, while estradiol develops the characteristic blue color, following Beer's law over a wide range. Serum or serum diluted with 6% bovine albumin is incubated with estradiol benzoate (0.2 mg. per cc.), which is added in ethanol so that final ethanol concentration is below 10%. Serum heated for one hour at 63° serves as a control for enzyme activity. Heated and unheated sera without substrate serve as controls for sera constituents reacting with the phenol reagent. The reaction is ended by precipitation at 80 to 90% ethanol concentration, removing the proteins which would react with the phenol reagent.

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(1) Aided by a grant from the Donner Foundation, Incorporated.

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(4) F. Bischoff, R. E. Katherman and J. J. Moran, Abst. 115th Meeting Am. Chem. Soc., 1949, p. 6C.