hydrogen bonding and other effects. A review of available results (*1, 2, 4*) indicates that

$$\Delta pK = pK^{D} - pK^{H} = 0.45 + 0.015\ pK^{H} \qquad (9)$$

is an approximate representation for $-5 < pK < 16$ with wide aberrations on both sides of the line. From $-5 < pK < 16$ all recorded values are within $0.15 < \Delta pK < 0.8$. Ionizations from carboxylic acids with positive charges such as glycine fall below the line while those with negative charges lie above the line of Eq. 9. Since H_2O is a 5 times stronger acid than D_2O, it also lies near the line of Eq. 9, but the 1.5 times greater acidity of H_3O^+ over D_3O^+ (*5*) falls far below the line and is nearly the lowest ratio recorded.

Some of the greatest deviations from the line of Eq. 9 are given by carboxylic acid ionizations. By explicitly considering charge type and adding a term to Eq. 9, agreement with observed values is markedly improved. For carboxylic acid ionizations only, Eq. 10 is suggested, where Z denotes the net charge on the acid form of the conjugate acid-base pair that is being considered.

$$\Delta pK' = 0.45 + 0.015\ pK^{H} - 0.12Z \qquad (10)$$

For instance, for three ionizations from citric acid (*2*), $pK_1{}^{H} = 2.95$, $pK_2{}^{H} = 4.38$, and $pK_3{}^{H} = 5.80$. From Eq. 9, $\Delta pK_1 = 0.49$, $\Delta pK_2 = 0.52$, and $\Delta pK_3 = 0.54$. Equation 10 gives $\Delta pK_1' = 0.49$, $\Delta pK_2' = 0.64$, and $\Delta pK_3' = 0.78$, in much better agreement with the observed differences (*2*) of 0.49, 0.64, and 0.75, respectively. Neutral acids such as acetic acid which are nearly on the line of Eq. 9 give, of course, the same difference when Eq. 10 is used. If an equation of the form of Eq. 10 had been used in place of Eq. 1 for carboxylic acid ionizations, the same result, $b_1 = b_2$, would have been obtained if both ionizations were from carboxylic acid groups because terms in Z and $(Z-1)$ would cancel. The numerical value of the "pre-Z" factor, 0.12 in Eq. 10, may be dependent on ionic strength. The ΔpK values for citric acid quoted are at about 0.1 ionic strength. It would be of interest to learn the differences upon extrapolation to zero ionic strength.

No numerical values of charge-type factors, such as appear in Eq. 10 for carboxylic acids, are suggested for other acidic groups because fewer results with a variation in charge type have been recorded. The limited data suggest, however, that the numerical value would be less for ammonium ionizations. It is suggested that charge-type factors will prove important only where charge separations occur as in carboxylic acid and phenol ionizations and not in proton transfers such as occur in ammonium ions. Substitution of Eq. 10 for carboxylic acid ionizations and Eq. 9 or some other equation with a zero or lesser "pre-Z" factor than Eq. 10 for ammonium ionizations in molecules such as glycine with two different acidic groups yields nonequal slopes differing by the difference of their "pre-Z" factors, for the two kinds of acid groups. Too few points are available to test this hypothesis, but all points for such carboxylic acid ionizations lie below the line of Eq. 9. As an example, for the carboxylic acid ionization from glycine with a positive charge on the acidic form of the molecule and $pK_1{}^{H} = 2.47$, application of Eq. 10 yields

$$pK_1 = 0.45 + 0.04 - 0.12 = 0.37,$$

which compares favorably with the observed (*2*) value of 0.39. For the ammonium ionization from glycine from a molecule with $pK_2{}^{H} = 9.65$ we apply Eq. 9 to obtain $pK_2 = 0.45 + 0.15 = 0.60$ in good agreement with the observed (*2*) value of 0.63. For triglycine, however, with $pK_1{}^{H} = 3.28$ Eq. 9 gives better agreement with the experimental difference (*2*) of 0.47 indicating that charge separation also plays a role in determining ΔpK.

Even though this last section has emphasized a probable role for charge type in determining ΔpK, many other factors such as bond type undoubtedly enter this complex quantity (*6*).

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Alkanes in Natural and Synthetic Petroleums: Comparison of Calculated and Actual Compositions

Abstract. *A similarity exists between the low molecular weight alkane isomers in crude oil and Fischer-Tropsch catalytic synthesis products. The composition of the C_4 through C_7 alkane isomers in a crude oil was calculated quantitatively with the equations previously used to calculate the alkane isomers in Fischer-Tropsch products. These results may have significance in ascertaining the origin of the volatile hydrocarbons in crude oils.*

Practically all present hypotheses on the origin of petroleum propose that the source materials were the remains of plants and animals (*1*). Early experiments pointed to inorganic origins in the earth (*2*). These theories have been mainly displaced, but proponents still exist (*3, 4*). Robinson (*4*) has proposed that petroleum consists of primeval oils of unknown source that became admixed with oils from organic life. The proposed primeval oils might possibly have arisen by catalytic syntheses such as the Fischer-Tropsch synthesis. This is a catalytic reaction of CO and H_2 at about 170° to 330°C at atmospheric or higher pressures, that produces complex mixtures of hydrocarbons and oxygenated derivatives from C_1 to waxes of high molecular weight. The hydrocarbons include paraffins, olefins, naphthenes, and aromatics.

We have noted a similarity between the concentrations of the alkane isomers in crude oils (*5, 6*) and the concentrations in hydrogenated Fischer-Tropsch synthesis products (*7–11*). Table 1 (*i*) illustrates this similarity for the C_6 and C_7 branched alkanes. In both products a reversal occurs for the methyl derivatives: the concentration of 2-methylpentane is greater than that of 3-methylpentane, and the concentration of 2-methylhexane is less than that of 3-methylhexane. Recent data from 11 of 14 crude oils examined also show this reversal (*12*). One of the unique results found in the analysis of Fischer-Tropsch products (*7, 8*) was this same reversal.

The comparison of Fischer-Tropsch and petroleum components in Table 1, (*i*) is not very quantitative. Unfortunately there are no detailed analyses of

Table 1. Alkane compositions: crude oil and Fischer Tropsch product (F.T.). Units are mole percent (gram-moles per 100 gram moles. Horizontal lines in the body of the table signify a total of 100 mole percent for each group of alkanes.

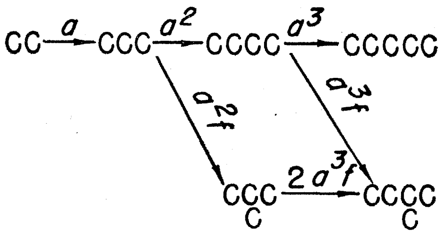
Alkanes	(*i*) Observed C_6 and C_7 branched alkanes (*8, 11*)		Isomer distribution						
			(*ii*) F.T. (*8, 11*)			(*iii*) Crude oil from modified F.T. equations			
	No. 1 Crude (*6*)	F.T.	Observed	Predicted $f = 0.0727$		Observed No. 1 (*6*)		Predicted $f = 0.176$	
n-Butane			89.4	93.2	a^2	87.4		84.8	
2-Methylpropane			10.6	6.8	a^2f	12.6		15.2	
n-Pentane			81.2	82.1	a^3	65.8		65.3	
2-Methylbutane			18.8	17.9	$3a^3f$	33.8		34.5	
2,2-Dimethylpropane						0.4		0.2	
n-Hexane			78.8	73.2	a^4	56.6		49.6	
2-Methylpentane	53.9	53.1	11.2	15.9	$3a^4f$		53.9†		52.0†
3-Methylpentane	38.8	45.0	9.5	10.5	$2a^4f$		38.8		40.7
2,3-Dimethylbutane	6.7	1.9	.4	.4	$2a^4f^2$		6.7		6.1
2,2-Dimethylbutane	0.6	—					0.6		1.2
						43.4*	100	50.4*	100
						100		100	
n-Heptane			66.0	64.6	a^5	56.4		37.7‡	
2-Methylhexane	35.6	38.4	13.1	14.0	$3a^5f$		35.6†		31.9†
3-Methylhexane	45.6	56.	19.1	18.7	$4a^5f$		45.6		46.3
2,3-Dimethylpentane	11.7	4.7	1.6	2.0	$6a^5f^2$		11.7		11.9
2,4-Dimethylpentane	3.2	0.9	.3	.7	$2a^5f^2$		3.2		3.8
3-Ethylpentane	2.5	—					2.5		4.4
2,2-Dimethylpentane	0.7	—					0.7		0.7
3,3-Dimethylpentane	0.5	—					0.5		0.8
2,2,3-Trimethylpentane	0.2	—					0.2		0.2
						43.6*	100	62.3*	100
						100		100	
n-Octane			61.0	57.1	a^6				
Methylheptanes			36.4	37.4	$9a^6f$				
Dimethylhexanes			2.6	5.4	$18a^6f^2$				

* Total branched isomers. † Breakdown of the total branched isomers into mole percent (gram-moles per 100 gram-moles) of the individual branched isomers. ‡ For $f = 0.10$, calculated and observed values respectively are: for nC_7 56.1 and 56.4; and for isoC_7's 43.9 and 43.6.

Fischer-Tropsch products which have as extensive branching as petroleum components. But calculation methods developed in Fischer-Tropsch studies permit closer comparisons.

The Fischer-Tropsch synthesis is not an equilibrium process. The nature of the products is at least partly determined by the reaction mechanism; on this premise quantitative calculations of compositions have been made (*7–10*). Simple rules have been used to predict both the hydrocarbon-isomer distribution and carbon-number distribution data. Anderson, Friedel, and Storch considered simple kinetic pictures of chain growth where there were stepwise additions of one carbon atom (*8*) at end- or adjacent-to-end carbon atoms of the growing chain. Addition was not postulated to occur on any carbon atom that would result in producing structures containing ethyl branches or quaternary carbons, because such compounds were not found in early analyses of Fischer-Tropsch products. The particular scheme of addition used to obtain the data in Table 1, (*ii*) is: Addition may occur at only one end of the growing chain on any end carbon, or on any adjacent-to-end unsubstituted carbon (*8*). The reversal of 2- and 3-methyl derivatives is quantitatively reproduced.

The equation for calculation of isomer distribution is $\phi_n = kF_n a^{(n-2)}$, where ϕ_n is the number of moles containing *n* carbon atoms, *k* is a constant and F_n is a function of *f*, a constant representing the ratio of chain branching, *b*, over chain lengthening, *a*. If $b = af$, the lengthening and branching of chains is illustrated as follows:



Values for the relative concentrations of the isomers in terms of *a* and *f* are given in Table 1, (*ii*).

Calculations based on the equations for prediction of the products of synthesis have now been applied to some crude oils; high *f* values were chosen because of the greater branching. With no modification of the Fischer-Tropsch equations the predicted values are quite good for C_4 through C_7 alkanes from a paraffinic Saudi Arabian crude oil (No. 1 from *6*). However, the very good comparison in Table 1, (*iii*) was obtained after removing restrictions on the formation of quaternary carbon groups and ethyl branches. The petroleum hydrocarbons definitely include small concentrations of such compounds (for example, 2,2-dimethylpentane and 3-ethylpentane); in fact, recently 3-ethylpentane has also been observed in a Fischer-Tropsch product (*13*). The less restrictive conditions are: Addition of a carbon atom is permitted on the first three carbon atoms, or on alkyl groups attached to them, on one end of a growing chain; the branching factor is *f* as usual except in the formation of quaternary carbons, in which case 0.1 *f* is used because of the low probability of substitution on tertiary carbon atoms.

The total distributions for normal and branched isomers within each carbon group are more comparable only if the value of *f* is decreased with increasing carbon number (Table 1, (*iii*) and footnotes). Similarly, there is an indication from recent analyses of Fischer-Tropsch products, that the *f* number also must be decreased with increasing molecular weight in order to fit the observed distribution (*9*).

The similar alkane compositions in crude oil and synthesis products indicate that synthesis reactions from simple molecules, not necessarily Fischer-Tropsch reactions, might have contributed to petroleum. The products from the synthesis could have formed the initial portions of petroleum beds, which at later periods remained at low temperatures and accumulated materials from organic sources (*4*). A petroleum bed originating from synthesis reactions could contain from the beginning the full range of molecular weights observed in crude oils.

The present results do not constitute evidence for an inorganic origin of petroleum; the results indicate only that the volatile components of crude oils could have originated from synthesis reactions. The data cannot exclude other possible origins such as bacterial degradation, thermal reactions, and so forth, for which detailed comparisons of volatile components are needed (*14*).

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Chelation of Calcium by Lactose: Its Role in Transport Mechanisms

Abstract. *Lactose, like other sugars and polyols, prevents or delays the precipitation of calcium ion in the presence of bicarbonate buffer. That an uncharged calcium-lactose complex is formed was demonstrated by the use of paper electrophoresis and of calcium-45 as a label for the complex. Enhancement of the intestinal absorption of calcium ion by sugars could result from a complex of low molecular weight.*

The effect of dietary factors, especially sugars and amino acids, on the gastrointestinal absorption of calcium and other alkaline earth metals is well documented (*1*). Of the sugars tested, lactose has been found to be most effective (*2*). Despite extensive experimental study of intestinal microflora, influence on the *p*H of the intestinal tract, and the higher osmotic or hydrostatic pressures induced by the hypertonic solutions of sugars, no adequate theory of the mechanism of this absorption has been proposed. Lactose must therefore operate directly in the lumen of the intestine since it must be present simultaneously with the calcium in order to manifest its activity. Lactose, injected intravenously or present in another segment of the intestine, has no effect on the absorption of Ca^{++} (*3*).

Polyhydroxy compounds, particularly reducing sugars, form stable, soluble complexes of low molecular weight with metal ions (*4*). Furthermore, one of these compounds, the iron-fructose chelate, rapidly induces the deposition of iron in spleen and liver when administered orally to rats (*5*).

It is assumed that, within the intestinal lumen, calcium enters from the acid environment of the stomach as a free ion. As the *p*H is raised, a small portion of the metal is directly bound and transported by sites on or in the mucosal membrane. A major fraction is precipitated as an insoluble salt or complex, such as the carbonate, phosphate, oxalate, acylates of fatty acids, and so forth. We propose that the mechanism by which the sugars promote the absorption of Ca is by the formation of a complex with the metal whereby a soluble form of Ca^{++} is readily available for transport.

The ability of various sugars to prevent or delay precipitation of calcium as the carbonate was studied, since bicarbonate is the principal anion in the intestinal lumen (*6*). Measurement of the rate of formation of $CaCO_3$ by turbidimetric methods yielded inconsistent results because of the difficulty in obtaining precipitates with uniform characteristics and dispersion. However, qualitatively, it was easily shown that a molar ratio of 40:1 of lactose to Ca^{++} delays, if it does not prevent, the appearance of precipitate for extended periods of time.

The rate of precipitation of $CaCO_3$ was measured quantitatively in the following manner. Stock solutions of sugars (0.4*M*), $CaCl_2$ (0.2*M*), and $NaHCO_3$ (1.0*M*), were prepared from analytical grade reagents. With continuous stirring, 20 ml of the sugar solution and 1.0 ml of the $CaCl_2$ were mixed, and the *p*H was monitored with a *p*H meter. Initial *p*H of the solution was 6.50. The reaction was started by adding 0.5 ml of the $NaCHO_3$ solution. There was an immediate rise of *p*H to 7.65. The rate of reaction was followed by the fall of *p*H according to the equation

$$Ca^{++} + HCO_3^- \rightleftharpoons CaCO_3 + H^+.$$

As a control, 20 ml of H_2O was used. The results of a typical experiment, comparing the activity of lactose and fructose, are presented in Fig. 1. Initial rates of preciptation can be obtained by extrapolating the curves to zero time and measuring their slopes. The sugars and polyols, in order of decreasing effectiveness in delaying precipitation are: lactose > ribose > fructose = mannose > glucose > sorbitol = mannitol = sucrose.

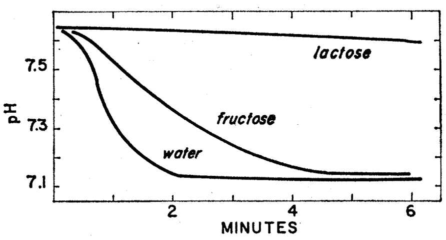

Fig. 1. Rate of H^+ liberation during formation of $CaCO_3$ by Ca^{++} in the presence of HCO_3^- buffer, without sugar and with fructose and lactose.

The calcium-lactose complexes were studied by paper electrophoresis. To 1.0 ml of $CaCl_2$ (0.01*M*) was added 10 μl of $Ca^{45}Cl_2$, whose activity was 1.5 mc/ml (obtained from Oak Ridge National Laboratory). A two-chambered electrophoresis apparatus was used; in one compartment the buffer solution was 0.05*M* $NaHCO_3$ at *p*H 7.0 and, in the other, 0.05*M* $NaHCO_3$ plus 0.4*M* lactose, at *p*H 7.0. The paper strips were soaked in their respective buffer solutions, and a 0.1 aliquot of radioactive $CaCl_2$ solution, approximately 600 count/min, was applied to the origin of each. The strips were subjected to electrophoresis for 18 hours at 450 volts, 5 ma, 2°C. They were removed, dried, and analyzed for radioactivity with a Forro strip scanner and recorder. The migration patterns of the Ca^{45}, with and without lactose present, are shown in Fig. 2. Lactose, in the absence of Ca^{++}, migrates to the same position as

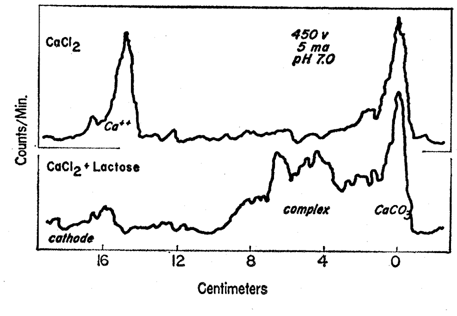

Fig. 2. Paper-electrophoretic migration of Ca^{45} in the presence and absence of lactose. The complex has no net charge and migrates at the same rates as lactose because of endosmotic flow.