Therefore, the assumption of an invariant rate constant, if incorrect to any degree, would result in a thermal correlation that is not as satisfactory as a diffusional correlation. However, beyond this point it is impossible to state whether the difference in correlation is due to the fact that either the reaction rate constant in the thermal equation is more affected by hydrocarbon or that the thermal mechanism less closely predicts the true combustion phenomenon.

Simon[2] has plotted the variation in burning velocity solely as a function of flame temperature and has remarked on the good correlation obtained. It is interesting to note that equation (2) predicts directly the variation in burning velocity with flame temperature if the mole ratio, n_1/n_2, is assumed independent of hydrocarbon–air mixture. This is a justifiable approximation since, near the stoichiometric mixture where maximum burning velocity occurs, the ratio rarely varies by more than two per cent. from the mean. Figure 1, then, is a log–log plot of burning velocity predicted by equation (2), using the experimental value of propane as a basis, *versus* the calculated equilibrium flame temperature with n_1/n_2 a constant. The equation plots essentially as a straight line predicting that the burning velocity varies approximately as the 4.9 power of the flame temperature. Disregarding the burning velocities of ethylene and acetylene, which give anomalous results with both theories, the rate of change of burning velocity with equilibrium flame temperature is satisfactorily predicted by the modified Semenov equation. It is not certain whether the fact that the predicted rate of change is not quite as great as actually occurs is due to the choice of a slightly low average activation energy, to a progressive increase of the frequency factor with decreasing chain length of the alkynes or to an activation energy for the alkynes that is progressively lower than the assumed value. However, it would not seem to be due to the selection of a low average activation energy for two reasons. First, the trend of the alkynes with decreasing chain length appears to be toward lower activation energy and higher frequency factor, as is exemplified in acetylene. Second, since the activation energy value selected was from available data on low temperature hydrocarbon oxidation, it would be expected that the value would be too high rather than too low when applied to activation at combustion temperatures.

A variation of less than 5% in activation energy will bring the calculated burning velocities, as shown by the modified Semenov equation, in line with experimental values for all mixtures except ethylene and acetylene. This is an indication that the initial assumption of the constancy of the frequency factor and activation energy was justifiable. Furthermore, it again stresses the fact that both thermal and diffusional theories indicate a marked similarity of most hydrocarbons for the combustion reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

Physical Properties of Perfluoro-*n*-hexane and Perfluoro-2-methylpentane

BY VERNON E. STILES AND GEORGE H. CADY

RECEIVED MARCH 8, 1952

Samples of two isomeric perfluorohexanes have been prepared by the fluorination of the pure hydrocarbons with cobalt trifluoride. The resulting crude products were fractionally distilled and the best cuts of each were combined. These were used for determinations of melting point, vapor pressure, surface tension, viscosity, density and index of refraction. Of the two compounds the normal fluorocarbon is the less dense, the less viscous and the more volatile. Its surface tension and index of refraction are the lower. The liquids are very much alike, but their physical properties differ from each other somewhat and in directions opposite to those for the corresponding hydrocarbons. In this respect they resemble perfluoro-*n*-pentane and perfluoroisopentane.

While it is well known that fluorocarbon isomers closely resemble each other in many ways, it is still the case that only a few specific examples may be cited as evidence for this generalization. The most thoroughly studied example is that of perfluoro-*n*-pentane *vs.* perfluoro-isopentane.[1–5]

A number of properties of two isomers of perfluorohexane are reported in this paper.

Experimental

Preparation of Fluorocarbons.—These compounds were prepared by the fluorination of hydrocarbons with cobalt trifluoride using the apparatus and procedures of Barber, Burger and Cady.[1]

The hydrocarbons were of high quality, being Research Grade products of the Phillips Petroleum Company. Analyses reported by the Company were: *n*-hexane, 99.85 ± 0.05 mole %; 2-methylpentane, 99.74 ± 0.06 mole %. It is assumed that the predominant perfluorohexanes in the products were of the same structure. Following the fluorination of the hydrocarbons, the resulting crude fluorocarbons were refluxed with an alkaline solution of potassium permanganate, to remove unsaturated compounds, and were then carefully distilled using a fractionating column shown under test to have about 82 theoretical plates. During the distillations cuts of about 10-ml. volume were taken, and those from the middle region of each distillation temperature plateau were later combined. Such blended samples were used for the determination of physical properties other than the melting points.

From 217 g. of *n*-hexane about 585 g. of crude fluorocarbon boiling above 50° was obtained. The distillation yielded 245 g. of a "plateau" product having a head temperature range from 57.08 to 57.30°. Fractions having a distillation range from 57.11 to 57.12° were combined to make the sample used for studies of physical properties.

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From 520 g. of crude fluorinated 2-methylpentane, 230 g. of a "plateau" product of distillation range 57.38 to 57.74° was obtained. Cuts taken from 57.65 to 57.66° were combined to give the 28-ml. sample used for physical measurements.

Physical Properties.—Apparatus and the procedures developed for studying the perfluoropentanes were employed for the two hexane fluorocarbons. Melting points were obtained from warming curves; boiling points and heats of vaporization were calculated from vapor pressures; densities were measured with pycnometers; viscosities were determined with a Ubbelohde viscometer; refractive indices were found by using a fluorocarbon filled prism in a spectrometer; surface tensions were measured by the capillary rise method.

Melting Point.—Warming curves for samples widely separated on the distillation plateau for perfluoro-*n*-hexane indicated melting points of −86.05, −86.20 and −87.1°, respectively. The highest of these values is probably the best, for impurities, when present, would lower the melting point. No transition was observed at temperatures above −180°. From the shape of the warming curve the molar entropy of fusion of the solid was estimated to be about 23 cal./degree. The temperature range over which fusion appeared to take place, as indicated by the warming curve, suggests that the sample may have contained up to 4.5 mole % of impurities. If such impurities were present they were probably perfluorohexanes. Perhaps some isomerization occurred as the fluorination reaction took place. Hydrogen fluoride, a reaction by-product, is known to be a catalyst for isomerization of hydrocarbons.

TABLE I

PROPERTIES OF PERFLUORO-*n*-HEXANE

Temperature, °C.	Density, g./cc.	Vapor pressure, mm.	Surface tension, dynes/cm.	Viscosity, millipoises
0.00	1.7560			9.79
10.00	(1.7282)		(12.85)	(8.29)
10.03			12.88	
10.10	1.7270			
11.23		116.1		
13.02		126.2		
13.04		126.4		
20.00	(1.6995)		(11.92)	(7.10)
20.20		176.8		
20.21			11.88	
20.32				7.07
21.46	1.6948			
24.90		217.9		
29.55				6.18
30.00	(1.6695)		(10.98)	(6.14)
30.02			10.93	
30.10	1.6696			
33.49		313.5		
36.70		357.3		
39.98				5.35
40.00	(1.6387)		(10.05)	(5.35)
40.06	1.6384			
40.23			10.05	
40.64		416.5		
43.45		463.8		
46.28		515.6		
48.86		567.6		
49.96				4.68
50.00	(1.6064)		(9.11)	(4.71)
50.07	1.6070			
50.31			9.07	
52.00		634.1		
54.73		697.5		
57.00		754.2		
57.02		755.4		
62.97		919.1		
66.19		1020.2		
69.19		1121.3		

Warming curves on different samples of perfluoro-2-methylpentane were smooth and showed no irregularity corresponding to transition or fusion of the substance above −183°. Visual observation permitted one to see that the substance changed from a brittle glass to a very viscous liquid over a temperature range from about −140 to −136°. The failure to find a freezing point at a temperature above −100° together with the gradual rise in head temperature during the distillation of the crude product may constitute evidence that the substance was not pure. Perhaps it contained a few per cent. of other isomers formed by rearrangement of the carbon skeleton of the molecule.

Most of the physical constants reported in this paper should not be influenced very much by the impurities which may have been present.

Other Properties.—Tables I to III present other data. Those values which have been estimated from smooth curves drawn through experimental points are enclosed in parentheses.

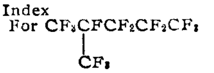
TABLE II

PROPERTIES OF PERFLUORO-2-METHYLPENTANE

Temperature, °C.	Density, g./cc.	Vapor pressure, mm.	Surface tension dynes/cm.	Viscosity millipoises
1.57				10.65
4.38		81.40		
10.00	(1.7610)		(13.3)	(9.23)
13.16	1.7505			
17.25		151.9		
20.00	(1.7326)		(12.38)	(7.87)
20.21	1.7319			7.86
21.48			12.26	
23.82		206.0		
29.20		259.3		
30.00	(1.7031)		(11.44)	(6.78)
30.10			11.41	
30.16	1.7026			6.77
33.37		308.3		
37.57		364.4		
39.98			10.49	
40.00	(1.6728)		(10.50)	(5.89)
40.39	1.6716			5.87
40.48		408.4		
43.57		458.9		
46.48		512.0		
49.92		579.2		
50.00	(1.6410)		(9.56)	(5.16)
50.07			9.58	
50.25	1.6402			
50.28				5.12
53.20		650.7		
55.40		703.1		
60.68		838.2		
63.65		924.5		
66.70		1018.3		
68.32		1071.2		

TABLE III

INDEX OF REFRACTION AT 22°

Light source	λ, Å	For n-C_6F_{14}	Index For  $CF_3\underset{CF_3}{\underset{\vert}{C}}FCF_2CF_2CF_3$
Na_D	5893	1.2515	1.2564
$Hg_{y\ 1,2}$	5780	1.2516	1.2565
Hg_g	5460.7	1.2519	1.2569
$Hg_{b.v.}$	4358.3	1.2545	1.2592
$Hg_{v.}$	4056.6	1.2554	1.2603

Vapor pressures for the two compounds correspond to the equations

$$\log_{10} P_{\mathrm{mm}} = 6.8637 - \frac{1075.6}{212.82 + t(^\circ\mathrm{C})} (\text{for } n\text{-}C_6F_{14})$$

$$\log_{10} p_{\mathrm{mm}} = 6.8825 - \frac{1093.77}{215.59 + t(^\circ\mathrm{C})}$$

(for perfluoro-2-methylpentane)

The normal boiling points for the two compounds as shown by vapor pressures are 57.23 and 57.74; respectively. Their molar heats of vaporization at the boiling points are 7307 and 7273 cal., and at 20° they are 7793 and 7740 cal. (Data for n-C_6F_{14} are given first in each case.) When calculating the heats of vaporization by the Clapeyron equation it was assumed that the vapors were ideal. Molar volumes of the liquids were obtained from their densities.

Discussion

These two isomeric perfluorohexanes compare with each other much as do perfluoro-n-pentane and perfluoroisopentane. The isomers are much alike but they differ from each other slightly in directions opposite to those for the corresponding hydrocarbons. Evidence appears to be accumulating that chain branching in fluorocarbons results in higher density, higher viscosity, higher boiling point, higher index of refraction and higher surface tension. Apparently the branched molecules can pack together more closely than the normal ones.

Acknowledgment.—This work was performed under contract with the Office of Naval Research, U. S. Navy Department.

SEATTLE 5, WASHINGTON

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

Polarography of Ethylenediamine Tetraacetate Complexes of Europium[1,2]

BY E. I. ONSTOTT

RECEIVED FEBRUARY 11, 1952

In the presence of a large excess of anions of ethylenediamine tetraacetic acid, europium(III) is reversibly reduced to europium(II) at the dropping mercury electrode in the pH range of 6 to 13.6. Complex ions identified from half-wave potential and diffusion current data are: pH 6 to 8, $[\mathrm{EuHY}]^{-1}$; pH 11 to 13.6, $[\mathrm{EuY}]^{-2}$; pH 6 to 8, $[\mathrm{Eu(HY)_2}]^{-3}$; pH 11 to 12, $[\mathrm{EuY_2}]^{-5}$; pH 13 to 13.6, $[\mathrm{EuY(OH)}]^{-2}$. Evidence is given for the existence of $[\mathrm{EuHY}]^{-1}$ and $[\mathrm{EuY(HY)}]^{-4}$, in the pH range of 8.5 to 10.3. The ratios of dissociation constants for several of the complex ions are calculated. The equilibrium constant for the reaction $[\mathrm{EuY_2}]^{-5} + \mathrm{OH}^- \rightleftarrows [\mathrm{EuY(OH)}]^{-2} + \mathrm{Y}^{-4}$ is calculated to be approximately 2.

Few of the known complexing agents are coördinated strongly to rare earth ions. Citrate has been used extensively in ion exchange separations,[3] and recently it has been shown that anions of ethylenediamine tetraacetic acid form stable complexes with rare earth ions.[4-8]

Of the rare earths which show oxidation states other than (III), europium and ytterbium appear to be the most suitable for studying complex formation by the polarographic method, since they are reduced to the (II) state at the dropping mercury electrode.[9-11] This report gives the results obtained in investigating the polarography of europium complexed by anions of ethylenediamine tetraacetic acid.

Laitinen and Blodgett[12] have used the dropping mercury electrode as an indicator electrode to show the presence of ytterbium(II) and absence of neodymium(II) when complexed by ethylenediamine tetraacetate.

For simplicity, the symbol proposed by Schwarzenbach and Ackermann[13] for ethylenediamine tetraacetic acid, H_4Y, will be used.

Experimental

Spectrographically pure europium oxide, obtained from Johnson, Matthey and Co., Limited, was weighed and dissolved in dilute hydrochloric acid to make a stock solution. The concentration of europium was based on the weight of the oxide after igniting at 900°. Ethylenediamine tetraacetic acid was precipitated from a solution of the sodium salt (Bersworth Chemical Co.) with concentrated hydrochloric acid, then recrystallized twice from 6 N hydrochloric acid, washed with alcohol and dried under a heat lamp. This product was weighed and dissolved in sodium hydroxide to give a stock solution. Sodium hydroxide was used for the reason that potassium hydroxide and tetrabutylammonium hydroxide gave irreversible reductions. Boric acid was used as a buffer for solutions having a pH of 8 to 10, and sodium dihydrogen phosphate was used for the pH range of 6 to 8. Citrate was not a suitable buffer, as irreversible behavior was observed when it was used. The ionic strength of the solutions was adjusted with sodium chloride. Sodium nitrate was tried as an indifferent electrolyte, but a reduction wave at about −1.5 volts when europium was present precluded its use.

A modified H-cell having a middle compartment separated by 20 mm. fine sintered glass discs was used. The first compartment and middle compartment contained the solution to be analyzed and in the third compartment was placed saturated potassium chloride, used as a bridge solution to a bulb type S.C.E. The a.c. resistance of the four cells used was 710, 990, 1500 and 1750 ohms, as measured with a General Radio impedance bridge in conjunction with the dropping mercury electrode and S.C.E.

A Sargent Model XXI polarograph was used to record polarograms. Potential measurements were made with a Rubicon Type B potentiometer. A Beckman Model G pH meter was used for pH measurements. For highly alkaline solutions, a Type E electrode was used.

The polarograph was operated manually. Average current data were taken along the polarographic wave and in

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[1] Work done under the auspices of the A.E.C.

[2] Data used in plotting the graphs in this article can be obtained by writing the author or by ordering Document 3612 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6 × 8 inches) readable without optical aid.

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