TABLE II

Quinone	Initial retarder concn. (*M*)	Radical concn. if only one monomer unit present	Radical concn. if five monomer units present
Anthraquinone	1.9×10^{-3}	2×10^{-3}	3×10^{-3}
Aminoanthraquinone	2.2×10^{-3}	1×10^{-3}	3×10^{-3}
Phenanthrenequinone	2.2×10^{-3}	1×10^{-3}	3×10^{-3}
Benzoquinone	1.9×10^{-3}	1×10^{-3}	3×10^{-3}
Naphthoquinone	2.5×10^{-3}	1×10^{-3}	2×10^{-3}
Chloranil	1.8×10^{-3}	1×10^{-3}	2×10^{-3}
Duroquinone	2.0×10^{-3}	3×10^{-3}	6×10^{-3}
Aurin tricarboxylic acid	7×10^{-2}	1×10^{-3}	2×10^{-3}
Indanthrene	1×10^{-3}	3×10^{-3}	5×10^{-3}

Assuming the simplest composition of the radical, that is, a benzoyl (or phenyl) fragment linked through only one monomer unit to a quinone residue, we obtain a molecular weight of about 300. In this case the apparent molar susceptibility would be

$$\chi_M = 0.005 \times 10^{-6} \times 300 = 1.5 \times 10^{-6}$$

But if *one* mole has a susceptibility of 1257×10^{-6}, then a "molar" susceptibility value of 1.5×10^{-6} will be exhibited by 1.5/1257 or 1×10^{-3} mole of radicals. Let us now assume that the radical has five monomer units. In this case its molecular weight will be 700 giving an apparent χ_M of 3.5×10^{-6} which is equivalent to a molar concentration of stabilized radicals of 3×10^{-3} *M*. Inasmuch as the original quinone concentration was 1.9×10^{-3} *M*, it would appear that the stabilized radicals are formed before the chain making up this stabilized radical has grown to more than five monomer units long (plus, of course, an initiator fragment) even if every molecule of quinone is used up in the formation of such radicals.

The idea that the stabilized radicals formed in quinone-retarded polymerizations are constituted from few monomer units has received support from the purely chemical study of Cohen.[19] He concludes that at low quinone concentrations (4.5×10^{-3} *M*, in his work) the chain growth process may be interrupted before the addition of a second monomer molecule.

It is, perhaps, not surprising that the amines and hydroquinone did not behave in the same fashion as did the quinones. Here the primary retarding step may be the abstraction of a hydrogen atom as postulated by Price[20] instead of direct addition to the retarder molecule. With aromatic nitro compounds, however, the reaction with aliphatic radicals has been considered to be nuclear addition resulting in a resonance stabilized species much like that visualized for quinone retardation. The evidence from the present work tends to cast some doubt upon close similarity of the two reactions. A possible alternative mechanism for the nitro compound retardation is that put forth by Bartlett[21,22] on kinetic grounds involving a radical which appears much less stable.

It is interesting to note that while an aromatic amine does not produce highly stabilized radicals, the amine group attached to a quinone, as in aminoanthraquinone and indanthrene, has no effect in preventing their formation. In each of these cases, however, the ring to which the amine group is linked has lost much of its aromatic character.

These results do not by any means disprove the theory of free radical intermediates in non-quinoid retardation. However, any radicals formed must be of an entirely different order of stability, the limits of detection of the present method being 10^{-4} to 10^{-5} *M* concentration of free radicals.

Acknowledgment.—We wish to thank Prof. P. W. Selwood of Northwestern University for helpful discussions during the early phases of this work.

[19] S. G. Cohen, *J. Polymer Sci.*, **2**, 511 (1947).

[20] C. C. Price, *Ann. N. Y. Acad. Sci.*, **44**, 351 (1943).

[21] G. S. Hammond and P. D. Bartlett, *J. Polymer Sci.*, **6**, 617 (1951).

[22] P. D. Bartlett and H. Kwart, THIS JOURNAL, **74**, 3969 (1952).

PRINCETON, N. J.

[CONTRIBUTION NO. 53 FROM THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING AND MANUFACTURING COMPANY]

The Effects of Structure on the Viscosities of Perfluoroalkyl Ethers and Amines

BY T. J. BRICE AND R. I. COON

RECEIVED DECEMBER 1, 1952

The viscosities of a number of fluorocarbons, cyclic and straight chain fluorocarbon ethers, and perfluoroalkyl tertiary amines have been measured over a range of temperatures. The oxygen and nitrogen-containing compounds have lower viscosities than fluorocarbons of the same type (cyclic or straight chain) and the same number of carbon atoms. Thermodynamic quantities related to viscous flow were calculated. Possible reasons for the viscosity effects observed are discussed.

The viscosities of a number of fluorocarbons have previously been measured, and in particular an extensive study of three perfluoropentanes has been made by Burger and Cady.[1]

The absolute viscosities and the temperature coefficients of viscosity of fluorocarbons are high compared to those of analogous hydrocarbons, hydrocarbon ethers (polyalkylene oxides) and siloxanes. The low viscosities and temperature coefficients of viscosity of the latter compounds have been attributed to high internal flexibility. This in turn has been attributed to progressively greater ease of rotation about the C–C, C–O, and Si–O bonds.[2,3] In siloxanes an additional factor is believed to be the ease of rocking of the $(CH_3)_2$-

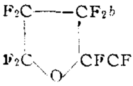
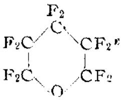
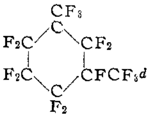
[1] L. L. Burger and G. H. Cady, THIS JOURNAL, **73**, 4243 (1951).

[2] A. Bondi, *J. Phys. Colloid Chem.*, **55**, 1355 (1951).

[3] C. M. Murphy and W. A. Zisman, *Ind. Eng. Chem.*, **42**, 2415 (1950).

TABLE I

PHYSICAL PROPERTIES OF SOME FLUOROCARBONS, PERFLUORO ETHERS AND PERFLUORO AMINES

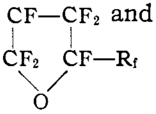
Compound	B.p., °C., (mm.)	$n^{25}{}_{D}$	$d^{25}{}_{4}$	η/d, 25° cs.	η, 25° cp.	Carbon		Fluorine		Mol. wt.		Liquid density equation
						Calcd.	Found	Calcd.	Found	Calcd.	Found	
n-C_5F_{12}[a]	29.3		1.6200 (20°)		0.4619 (24.9°)							
c-C_5F_{10}[a]	22.5		1.6451 (20°)		0.7670 (20.1°)							
 [b]	27.3 (743)	1.2502	1.6120	0.335	0.540	22.5	21.2	71.4	71.2	266	264	$d^t{}_4 = 1.6845-0.0029t$ (25 to −63°)
 [c]	33.4 (743)	1.2580	1.6625	.433	0.716	22.5	21.6	71.4	69.4	266	274	$d^t{}_4 = 1.7325-0.0028t$ (25 to −56°)
n-C_6F_{14}	56.1 (747)	1.2518	1.6771	.398	0.670	21.3	21.2	78.7	78.2	338		$d^t{}_4 = 1.7471-0.0028t$ (25 to −50°)
c-$C_6F_{12}O$	55.0 (731)	1.2628	1.6865	.470	0.802	22.8	22.8	72.2	72.4	316	315.5	$d^t{}_4 = 1.7540-0.0027t$ (25 to −50°)
$C_2F_5OC_2F_4OC_2F_5$	56-57	1.2392	1.5916	.373	0.592	19.5	19.7	71.9	70.6			$d^t{}_4 = 1.6616-0.0028.$ (25 to −50°)
n-C_8F_{18}	103.5-104 (725)	1.2675	1.7542	.713	1.250	21.9	22.0	78.1	77.7	438	434	$d^t{}_4 = 1.8192-0.0026t$ (80 to − 25°)
$(n$-$C_4F_9)_2O$	101.0	1.2607	1.7103	.655	1.118	21.2	21.3	75.4	74.3	456	454	$d^t{}_4 = 1.7712-0.0026t$ (80 to −25°)
c-$C_8F_{16}O$	102-103 (734)	1.2769	1.7602	.805	1.415	23.1	23.1	73.0	72.9	416	418	$d^t{}_4 = 1.8217-0.0026t$ (80 to −25°)
$C_8F_{16}O_2$	101-101.9	1.2721	1.7304	.743	1.285	22.2	22.5	70.4	70.0	432	435.5	$d^t{}_4 = 1.7906 - 0.0025t$ (80 to −25°)
$C_2F_5(OC_2F_4)_2$-OC_2F_5	94-96 (735)	1.2500	1.6311	.623	1.015	19.8	19.2	70.4	64.6	486	481	$d^t{}_4 = 1.7022-0.0029t$ (80 to −25°)
 [d]	101.5	1.2835	1.830		1.883							$d^t{}_4 = 1.897-0.0027t$
$C_2F_5N(C_3F_7)_2$[e]	110	1.2747	1.7809	.668	1.189							$d^t{}_4 = 1.8435-0.0025t$ (80 to −20°)
$(C_2F_5)_2NC_3F_7$[f]	90.5	1.2688	1.7537	.555	0.973							$d^t{}_4 = 1.8190-0.0026t$ (80 to −20°)

[a] L. L. Burger and G. H. Cady, ref. 1. [b] Freezes below −80°. [c] Freezes *ca.* −58°. [d] R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, 603 (1951). [e] N, calcd., 3.0; found, 2.7 [f] N, calcd , 3.3; found, 3.1.

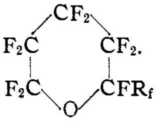
Si- group about the oxygen atoms due to the strongly ionic nature of the Si-O bond.[4]

Rotation about the C-C bonds in fluorocarbons is known to be hindered by a high energy barrier, 4350 cal./mole in C_2F_6,[5] as compared to 2700-3000 cal./mole in C_2H_6. This rigidity has been considered to be largely responsible for the viscosity properties of the fluorocarbons. On this basis it has been suggested that the viscosity and the temperature coefficient of viscosity of a fluorocarbon could be lowered by the insertion of –O– or $>NR_f$ (where R_f is a short fluorocarbon chain) into the carbon chain to provide greater internal flexibility.

The compounds used are listed in Table I. The data given for n-C_5F_{12}, c-C_5F_{10}, c-C_8F_{16} and c-C_9F_{18} were taken from the literature as indicated. The other compounds were prepared in these laboratories by the Simons electrochemical fluorination process from the appropriate organic compounds.[6] Their structures are self-evident except for those of c-$C_6F_{12}O$, c-$C_8F_{16}O$, and c-$C_8F_{16}O_2$. The first two are mixtures of α-substituted perfluorotetrahydrofurans,



and α-substituted perfluorotetrahydropyrans,



They are believed to be mostly the former. The structure of the c-$C_8F_{16}O_2$ is not definitely known, and may have two or only one of the oxygen atoms in the ring.

Experimental

The experimental data and analytical results are contained in Table I.

Purification of Materials.—The electrochemical cell products were first washed with strong aqueous base to remove entrained hydrogen fluoride. The fluorocarbon layer was separated and dried with phosphorus pentoxide. It was then fractionally distilled in a helix-packed column and center fractions of constant boiling point and refractive index taken for use. The purity of the samples was checked by elementary analysis and by infrared analysis.

Densities were determined in a Pyrex pycnometer consisting of a 5-ml. bulb to which was sealed a calibrated section of capillary tubing. Above the capillary was an expansion section of 8 mm. tubing. After the pycnometer had been filled through a vacuum system, the upper section was sealed. The liquid level in the capillary section above or below the calibration mark was read with a cathetometer. Corrections were made for the weight of vapor above the

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(4) E. G. Rochow, "Chemistry of the Silicones," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 115.

(5) E. L. Pace and J. G. Aston, THIS JOURNAL, 70, 566 (1948).

(6) J. H. Simons, "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950, p. 401.

liquid, expansion or contraction of the glass, and buoyancy of air.

The pycnometer bulb and capillary were calibrated with pure mercury at 25°. "International Critical Tables" values for the density of mercury were used.

Viscosities were determined with calibrated Cannon–Fenske viscosity pipets. Pure CCl_4 was used to check the calibration over the temperature range covered. The deviations from accepted values were found to be less than 2% at the extreme temperatures and about 1% from 0 to 50°. The greatest source of error probably arises from the slight differences between the temperature at which the pipet is charged and the temperature at which it is operated and the consequent change in driving head.

Temperature control for all constant temperature baths above 0° was obtained by the use of a "merc-to-merc" regulator; the temperature was held within $\pm 0.1°$. The bath liquids were water, up to 50°, and petroleum oil at higher temperatures. Temperatures below 0° were obtained by dissolving Dry Ice in acetone contained in a dewar flask. It was possible to control the temperature within $\pm 0.5°$ by periodic small additions of Dry Ice and constant stirring.

Boiling points were measured by the method described by Quiggle, Tongberg and Fenske.[7]

Molecular weights were determined by vapor density methods. The molecular weights of the C_5 and C_6 compounds were measured in a vapor density balance. The molecular weights of the C_8 compounds were determined by means of a Monel Dumas bulb. This bulb had a volume of about 50 ml. and was fitted with a Teflon-packed Hoke needle valve and a thermocouple well. In determining molecular weights, the bulb was first heated to constant weight in a hot air-bath equipped with a thermoregulator, cooled, evacuated and the liquid sample drawn in without admitting air. The bulb was then heated to the desired temperature, about 100° above the boiling point of the sample, and carefully vented down to atmospheric pressure. The bulb was then closed, cooled, reweighed and the molecular weight calculated on the assumption that the vapor behaved as a perfect gas. Measured molecular weights did not deviate from the theoretical values by more than 2%. The apparatus could be safely heated to 300°. The design was based on a suggestion of Dr. J. D. Park of the University of Colorado.

Refractive indices were obtained with a Spencer Abbe-type refractometer capable of readings from 1.2000 to 1.5000 with a precision of ± 0.0001.

Physical Properties. Boiling Points.—The perfluoro straight chain eight carbon ethers have markedly lower boiling points than n-C_8F_{18}. Their lower boiling points are hardly likely to be due to lower intermolecular forces since their polarizabilities are higher than that of n-C_8F_{18}, and this should lead to higher, not lower, intermolecular forces. However, an increase in the entropy of vaporization, ΔS_v, over the ideal case can lead to lower boiling points than are predicted from the intermolecular forces, since the boiling point is related to ΔS_v by $T_b = \Delta H_v / \Delta S_b$. Bondi has shown that such a boiling point lowering occurs with the fluorocarbons and siloxanes.[2] In the ideal case, molecules are assumed to rotate freely in the liquid state; greater order in the liquid, which an increase in ΔS_v implies, has been associated with restriction on the freedom of external rotation of molecules in the liquid. In the present instance, the C_8 perfluoro straight chain ethers may be considered to be less free to rotate externally than even the rigid fluorocarbon molecule and, consequently, to have slightly higher entropies of vaporization and lower boiling points than C_8F_{18}. Similar effects were shown by $C_6F_{14}O_2$ and the C_8 perfluoro cyclic ethers where the expected boiling point increase with increased molecular weight was not found.

Densities and Refractive Indices.—The densities of the perfluoro ethers are lower than those of the corresponding fluorocarbons. The temperature coefficients of density are all approximately 0.0025-0.0028 ml./ml./deg. This is the usual range for fluorocarbons.

The refractive indices of the perfluoro ethers are also lower than those of fluorocarbons with the same type of structure (cyclic or straight chain) and the same number of carbon atoms. The molar polarizabilities of the compounds were calculated; the polarizabilities of the perfluoro ethers are all higher than those of fluorocarbons having the same number of carbon atoms and the same type of structure.

Viscosities.—The perfluoro straight chain ethers have lower absolute viscosities than straight chain fluorocarbons having the same number of carbon atoms; the kinematic viscosities (η/d) of the perfluoro ethers are also lower, although not as much as the absolute viscosities, because of the lower densities of the ethers. Both the straight chain fluorocarbons and perfluoro ethers have lower viscosities than either cyclic fluorocarbons or perfluoro cyclic monoethers of the same number of carbon atoms.

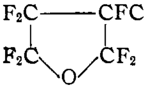
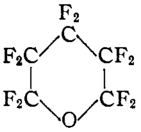
The perfluoro cyclic ethers have lower absolute and kinematic viscosities than cyclic fluorocarbons having the same number of carbon atoms.

The viscosities of the two isomers of c-$C_5F_{10}O$ are quite different from one another. This is not surprising, since their other physical properties also differ widely. The isomers of $C_6F_{12}O$ which were used in this work boil very close to one another, and their other physical properties would be expected to be very similar. This is also true of the c-$C_8F_{16}O$ mixture. The curve in Fig. 1 drawn for the perfluoro cyclic ethers would very likely be the same, if data for the individual isomers of the c-$C_6F_{12}O$ and c-$C_8F_{16}O$ mixtures were available and had been used.

TABLE II

VISCOSITIES

The viscosity, in poises, is obtained by substituting the proper values in the table in the equation: $\log \eta = (A/T) - B$.

Compound	A	B	Temp. range, °C.
	560.0	4.141	25 to −63
	605.0	4.158	25 to −56
n-C_6F_{14}	568.8	4.079	25 to −50
c-$C_6F_{12}O$	620.0	4.172	25 to −50
$C_2F_5OC_2F_4OC_2F_5$	598.0	4.229	25 to −50
n-C_8F_{18}	706.5	4.261	80 to −25
$(n$-$C_4F_9)_2O$	645.8	4.111	80 to −25
c-$C_8F_{16}O$	728.0	4.282	80 to −25
$C_8F_{16}O_2$	666.0	4.118	80 to −25
$C_2F_5(OC_2F_4)_2OC_2F_5$	659.9	4.200	80 to −25
$(C_2F_5)_2NC_3F_7$	641.7	4.159	80 to −20
$C_2F_5N(C_3F_7)_2$	663.5	4.139	80 to −20

Discussion

Viscosity as a Rate Process.—A number of thermodynamic quantities based on Eyring's rate process theory of viscous flow have been calculated and are given in Table III.

The activation energies for viscous flow (E_{vis}) which determine the temperature coefficients of viscosity were obtained from the slopes of $\log \eta$ *vs.* $1/T$ plots. These plots are straight lines, as nearly as could be determined, over the temperature ranges used; there is no evident variation of E_{vis} with temperature. Burger and Cady[1] have observed such variations, particularly at low temperatures.

The values of E_{vis} have been plotted in Fig. 1 as E_{vis} *vs.* molecular weight. For any one class of compound E_{vis} increases linearly with increasing molecular weight. The line V drawn through the E_{vis} value for $(C_4F_9)_2O$ connects this point with the E_{vis} of $(C_6F_{13})_2O$ (5.02 kcal./mole) which is beyond the limit of the graph. The E_{vis} values of both

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[7] D. Quiggle, C. O. Tongberg and M. R. Fenske, *Ind. Eng. Chem., Anal. Ed.*, **6**, 466 (1934).

TABLE III

THERMODYNAMIC QUANTITIES RELATED TO VISCOUS FLOW

Compound	B.p., °C.	E_{vis}, kcal./mole	$\Delta F^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.	ΔE_{vap}, kcal./mole (calcd.)	$\Delta E_{vap}/E_{vis}$	$\Delta vap/\Delta F^{\ddagger}$
$n\text{-}C_5F_{12}$[a]	29.3	2.24	3.14	−4.0	6.05	2.7	1.9
$c\text{-}C_5F_{10}$[a]	22.5	2.94	3.30	−2.4	5.76	2.0	1.7
	(Values for 20°)						
$\underbrace{CF_2CF_2CF_2CF}_{O}—CF_3$	27.3	2.56	3.25	−2.28	5.86	2.29	1.81
$\underbrace{CF_2CF_2CF_2CF_2CF_2}_{O}$	33.4	2.75	3.38	−2.05	5.99	2.18	1.77
$n\text{-}C_6F_{14}$	56.1	2.60	3.57	−2.95	6.43	2.47	1.80
$C_2F_5OC_2F_4OC_2F_5$	55.0	2.74	3.57	−2.50	6.39	2.33	1.79
$c\text{-}C_6F_{12}O$	55.0	2.84	3.62	−2.30	6.39	2.25	1.76
$n\text{-}C_8F_{18}$	103.5	3.24	4.25	−2.69	7.35	2.27	1.73
$(n\text{-}C_4F_9)_2O$	102.0	2.95	4.26	−3.48	7.32	2.48	1.72
$C_2F_5(OC_2F_4)_2OC_2F_5$	95.0	3.02	4.09	−2.90	7.19	2.38	1.76
$\overbrace{(CF_2)_3—\underset{CF_3}{C}FCF_2\underset{CF_3}{C}}F$[b]	101.5	3.45	4.38	−2.48	7.32	2.12	1.67
$c\text{-}C_8F_{16}O$	102.0	3.34	4.26	−2.46	7.32	2.20	1.72
$c\text{-}C_8F_{16}O_2$	102.0	3.05	4.31	−3.36	7.32	2.40	1.70
$C_2F_5N(C_3F_7)_2$	110.0	3.04	4.34	−3.40	7.48	2.46	1.72
$(C_2F_5)_2NC_3F_7$	92.0	2.94	4.14	−3.29	7.13	2.43	1.72
$1,3,5\text{-}C_6F_9(CF_3)_3$[c]	125.2	3.62					

[a] L. L. Burger and G. H. Cady, ref. 1. [b] Calculated from data of R. N. Haszeldine and F. Smith, *J. Chem. Soc.*, 603, (1951). [c] Calculated from data of A. V. Grosse and G. H. Cady, *Ind. Eng. Chem.*, **39**, 367 (1947).

straight chain and cyclic perfluoro monoethers are significantly, and about equally, lower than the E_{vis} values of fluorocarbons of the same structure and having the same molecular weight. The four lines (for straight chain and cyclic fluorocarbons and straight chain and cyclic perfluoro monoethers) appear to be converging toward a single curve. It seems reasonable that this should be true, since the special effects introduced by either a ring or a single oxygen atom would be expected to be overshadowed by the acyclic fluorocarbon portion of the molecule, as the molecular weights increase.

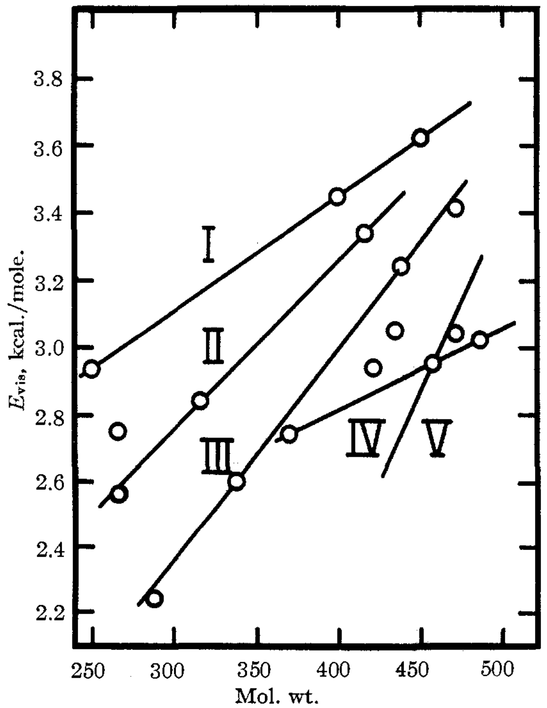

Fig. 1.—Activation energy for viscous flow as a function of molecular weight: I, cyclic fluorocarbons; II, perfluoro cyclic monoethers; III, straight chain fluorocarbons; IV, $C_2F_5(CF_2CF_2O)_nC_2F_5$; V, perfluoro straight chain monoethers. The points between III and V are for $(C_2F_5)_2NC_3F_7$ and $C_8F_{16}O_2$ (reading up). The point between IV and V is for $(C_3F_7)_2NC_2F_5$.

Of particular interest is the slope of the line connecting the E_{vis} values of $C_6F_{14}O_2$ and $C_8F_{18}O_3$. These compounds may be considered as the first two members of the series $C_2F_5O(C_2F_4O)_nC_2F_5$. It appears that for these compounds E_{vis} increases very much less rapidly with molecular weight than it does for the other compounds. If this is borne out by the higher members of the series, it would mean that at long chain lengths the temperature coefficients of viscosity would be very much less for this class of compounds than for fluorocarbons.

The two perfluoro tertiary amines have viscosities and temperature coefficients of viscosity close to those of perfluoro straight chain monoethers of the same molecular weight (Fig. 1). The effect of the single nitrogen atom in perfluoro tertiary amines falls off with increasing molecular weight. Thus the E_{vis} of $(C_4F_3)_3N$ is 4.90, about the same as that of $(C_6F_{13})_2O$.

The entropy of activation, $\Delta S^{\ddagger}$, which is a measure of the change in molecular orientation in going from the normal liquid to the activated state, was calculated for each compound on the assumption that

$$E_{vis} \cong \Delta H^{\ddagger}: \Delta S^{\ddagger} = (\Delta H^{\ddagger} - \Delta F^{\ddagger})/T$$

For most non-spherical organic molecules the activation energy for viscous flow has been found to be about one-fourth of the energy of vaporization, or $E_{vap}/E_{vis} \approx 4$. For all of these perfluoro compounds the E_{vap}/E_{vis} ratio was found to be considerably smaller, about 2.3 at the boiling point. This assumes that E_{vap} can be calculated reasonably well by using a Trouton constant of 21.5. If it is assumed that E_{vis} represents the energy necessary for the formation of a hole for the molecule that is moving, then this energy requirement is nearly twice that needed by organic compounds.

The ratio $E_{vap}/\Delta F^{\ddagger}$ approximates 1.7 to 1.8 for all of the compounds. For most organic compounds this ratio is 2.45.

Burger and Cady[1] found in the case of the perfluoropentanes that E_{vap}/E_{vis} at about the boiling point ranged from 2.0 to 2.7 and $E_{vap}/\Delta F^{\ddagger}$ from 1.7 to 1.9.

Effects of Oxygen Atoms.—The effect of the oxygen atoms in perfluoro straight chain ethers in producing compounds having lower viscosities and temperature coefficients of viscosity than fluorocarbons of the same molecular weight, could be explained by assuming that internal rotation about the carbon–oxygen bond is freer than rotation about carbon–carbon bonds, and that the ether molecule is thus more flexible and requires less energy of activation than the fluorocarbon. However, a comparison of the data on perfluoro cyclic ethers and perfluoro cyclic fluorocarbons shows that the oxygen atom is as effective in reducing the viscosities and temperature coefficients of viscosity in cyclic compounds as it is in the perfluoro straight chain monoethers. This is evident from the data in Table III and is illustrated in Fig. 1. It is difficult to see how ease of rotation about the C–O bond can have much meaning in these rigid ring compounds.

The similarity of the magnitude of the effects in the two classes of compounds suggests a common cause, and, since increased internal flexibility does not appear to explain the results on the cyclic compounds, it might be imagined that it is not the explanation for the results on the straight chain compounds either.

Effects of Nitrogen Atoms.—The effectiveness of the nitrogen atom in perfluoro tertiary amines in reducing viscosity and temperature coefficients of viscosity is about the same as that of the oxygen atom, judging by the data on $(C_3F_7)_2NC_2F_5$, particularly the relation of its E_{vis} to that of the normal fluorocarbons.

Acknowledgment.—We would like to thank Dr. P. W. Trott for the samples of the pure isomers of $C_5F_{10}O$, Mr. R. A. Guenthner for most of the other compounds, and Dr. H. E. Freier and Dr. W. E. Keiser of the Analytical Section for the numerous analyses.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Solvolysis Rates of Some Deuterated Tertiary Amyl Chlorides

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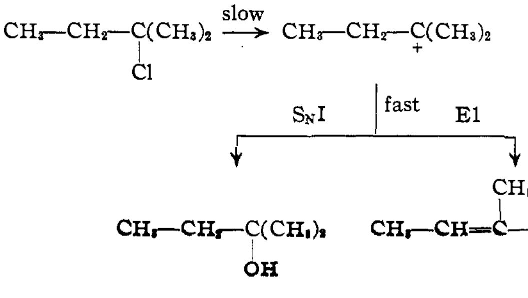
RECEIVED JANUARY 24, 1953

Three different β-deutero tertiary amyl chlorides, containing approximately 2, 6 and 8 deuterium atoms per molecule, have been synthesized and their rates of solvolysis and proportion of olefin formation in "80%" aqueous alcohol at 25° have been measured. The octa-deutero compound solvolyzed at a rate *ca.* two-fifths as fast as the undeuterated one while the less extensively deuterated compounds fell in the intervening range roughly spaced in proportion to the amount of β-deuteration. Deuteration of the methylene group was slightly more effective in reducing the rate than deuteration of a methyl group. Methylene deuteration cut the olefin proportion by a factor of *ca.* 1.5 while methyl deuteration showed no experimentally significant effect on this constant. This behavior is contrasted with that previously reported in a study of the effect of β-deuteration on the S_N2 and E2 reactions of isopropyl bromide. A tentative explanation in terms of mechanism is advanced to account for the reported isotope effects.

A logical extension of the recently reported work[2] on the isotope rate effect of deuterium substitution in the bimolecular reactions, S_N2 and E2, of a typical alkyl halide is the investigation of this effect in the solvolysis reaction in a case where conditions are known to be near limiting[3] or conducive to the unimolecular mechanism.[4] The present enigmatic state of our knowledge of this apparently simple but actually extremely complex organic reaction makes it, of course, the more interesting of the two cases. The theory of isotope rate effects has been presented in detail before[5-7] and experiments have confirmed that this is a particularly powerful tool in the investigation of reactions involving bonds between hydrogen and some other element, for it is in the case of the isotopes of hydrogen that the largest differences in zero point energies appear. The well-known Hughes-Ingold S_N1-E1 mechanisms at first sight appear to allow a simple prediction of the nature of the isotope effects in the reactions to which they pertain



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