The change from methyl to ethylcyclohexane is essentially similar to that from isobutane to isopentane, except for the symmetry number of three for isobutane. Consequently we have calculated the various thermodynamic functions for gaseous ethylcyclohexane from the equation

$$F(\text{ethylcyclohexane}) = F(\text{methylcyclohexane}) + F(\text{isopentane}) - F(\text{isobutane}) - R \ln 3$$

where F means C, S, $(H - H_0^0)/T$ or $-(F - H_0^0)/T$ and the $R \ln 3$ applies only to S and $-(F-H_0)/T$. This equation gives the value in Table VII.

By similar analogies one may offer equations for n-propyl and isopropylcyclohexane which may be of interest for making estimates.

$$F(n\text{-propylcyclohexane}) = F(\text{methylcyclohexane}) + F(\text{2-methylpentane}) - F(\text{isobutane}) - \text{R} \ln 3$$

$$F(\text{isopropylcyclohexane}) = F(\text{methylcyclohexane}) + F(\text{2,3-dimethylbutane}) - F(\text{isobutane}) - R \ln (3/2)$$

Again the $R \ln 3$ and $R \ln (3/2)$ terms apply only to the functions S and $-(F-H_0)/T$.

The values of several thermodynamic functions calculated by the various methods discussed above for a range of temperatures are listed in Tables X–XIII. Where values are given to the second decimal place, the error should not exceed 0.4, otherwise the error may be larger up to 1.0 or even more at the high temperatures.

These data of Tables X to XIII will be combined with the heat of formation values now being obtained by Rossini and collaborators in a later publication.

We wish to thank Dr. F. D. Rossini and Dr. H. M. Huffman for making available to us various data in advance of publication.

Summary

The data for cyclohexane from electron diffraction, Raman and infra-red spectra, and thermodynamic measurements were analyzed in various ways to give an assignment of vibration frequencies and calculated values of the heat capacity, entropy and heat and free energy functions for cyclohexane in the ideal gas state from 298.16 to 1500°K. It is concluded in agreement with others that at room temperature cyclohexane is predominantly in the chair form of symmetry D_{3d}. However, the heat capacity of gaseous cyclohexane definitely shows a contribution from conversion to the boat form which is approximately 5.6 kcal./mole higher in energy.

The possibilities of geometrical tautomerism in the methyl and dimethylcyclohexanes, mentioned in earlier publications, are discussed in greater detail. It is shown that the energy differences between these tautomers are related to the strain or steric energies in n-paraffins, and that there is good agreement between the corresponding energy quantity obtained from data on each series of compounds. The heats of isomerization confirm the assignment of the configuration *cis*-1,3-dimethylcyclohexane to the isomer boiling at 120.1° and *trans*-1,3 to the isomer boiling at 124.5°. The thermodynamic functions mentioned above were calculated also for methyl, ethyl and the seven dimethyl-cyclohexanes in the ideal gas state from 298.16 to 1500°K.

BERKELEY, CALIF. RECEIVED MARCH 12, 1947

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Phosphorus Fluoroisocyanates and Difluoroisothiocyanate

BY HERBERT H. ANDERSON

Studies of mixed halides containing fluorine and isocyanate or isothiocyanate have been undertaken in this Laboratory; the silicon fluoroisocyanates[1] have been described. This paper in turn presents phosphorus fluorodiisocyanate, difluoroisocyanate and difluoroisothiocyanate.

Phosphorus Fluoroisocyanates

Preparation.—A mixture of powdered, sublimed antimony trifluoride and phosphorus isocyanate (free from benzene or chloroisocyanates[2,3]) was heated gently in a single-necked flask to start the uncatalyzed reaction. Manual agitation was used, since the antimony isocyanate that formed neither melted nor dissolved and so produced a somewhat viscous mixture. The method resembles that employed in two closely related fluorinations.[1,4] Table I shows the proportions of the reagents used to produce the two mixed halides.

TABLE I

PREPARATION OF PHOSPHORUS FLUOROISOCYANATES, USING 50 G. OF ANTIMONY TRIFLUORIDE

Run	Starting liquid, g.	Reflux temp., °C.	Press., mm.	PF_2-(NCO), g.	PF-$(NCO)_2$, g.	Effective fluorine transfer, %
1	145 $P(NCO)_3$	80–90	140	6	48	75
2	53 $P(NCO)_3$	36–40	140	2.5	28	30
3	70 $P(NCO)_3$	90–92	760	15	29	60
4	94 $PF(NCO)_2$	50–60[a]	760	50	..	55

[a] Reaction required two hours.

Phosphorus fluorodiisocyanate was purified, utilizing distillation columns similar to the one recommended by Rose,[5] yielded material of b. p. 98.9–99.1° at 771 mm.; no rearrangement to form products such as phosphorus trifluoride, difluoroisocyanate and isocyanate could be detected at this temperature.

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[1] Forbes and Anderson, THIS JOURNAL, **69**, 1241 (1947).

[2] Forbes and Anderson, *ibid.*, **62**, 761 (1940); **65**, 2271 (1943).

[3] Anderson, *ibid.*, **64**, 1757 (1942); **67**, 223, 2176 (1945).

[4] Schumb and Anderson, *ibid.*, **58**, 994 (1936).

[5] A. Rose, *Ind. Eng. Chem.*, **28**, 1210 (1936).

TABLE II

PHYSICAL PROPERTIES OF PHOSPHORUS FLUOROISOCYANATES AND FLUOROISOTHIOCYANATE

Compound	$PF(NCO)_2$	$PF_2(NCO)$	$PF_2(NCS)$
B. p., °C.	98.7 ± 0.3	12.3 ± 1	90.3 ± 0.3
F. p., °C.	−55.0 ± 1.0	*ca.* −108	Glass; solid −95° f. p.
Density $^{20}{}_4$	1.475	~1.444[a] (3)	1.452
$n^{20°}$, white light	1.4678	1.3695 4.4° 1st time 1.3700 2.2° 2nd time	1.4978
Heat of vapn., cal.,[b] τ	9250	....	8080
Trouton Constant	24.8	....	22.2
Constants in log $P = A - B/T$	A 8.3210 B 2022.7	....	A 7.7045 B 1752.9
Error, av. mm.	±1.4	....	±1.9
Error, max. mm.	3.7		2.8
Stability	High	Low like $SiF_3(NCO)$ and PF_2Br	Fairly high
Solubility in CS_2	Critical soln. temp. about −16°	Limited, C. S. T. below b. p., ~0°	Unlimited above about −50°
Molar refraction, ml.	25.25	~17.38	Found 25.66, calcd. 25.72

[a] By buoyancy method using globe. [b] Obtained from vapor pressures.

Anal. Calcd. for $PF(NCO)_2$: N, 20.9; mol. wt., 134.06. Found (Dumas): N, 20.8; mol. wt., 138.

After hydrolysis, titration of the hydrogen of hydrofluoric acid plus the first hydrogen of phosphorous acid with methyl orange as indicator at *p*H 3.85 gave an equivalent weight of 66.4 ± 0.6 g., while the formula requires 67.0 g. Half of the alkali used corresponded to 14.3 fluoride; 14.2 calcd.

Phosphorus difluoroisocyanate was of limited stability and could not be purified by distillation in an all-glass vacuum system at either 0 or −35°. Evidently phosphorus trifluoride was constantly being formed at the expense of the difluoroisocyanate; yet samples of the difluoroisocyanate could be kept at 0° for a few days without much rearrangement. Distillation at low pressure favors decomposition, as does perhaps distillation under any circumstances. However, rapid distillation at 760 mm. yielded material of closely agreeing properties in two cases. Thus distillation of 20 g. of phosphorus difluoroisocyanate within ten minutes yielded material of b. p. 13.0–13.4° at 769 mm., with index of refraction 1.3695 at 4.4° in white light and a m. p. of about −108°. After standing overnight at −78°, a similar redistillation gave a main fraction of phosphorus difluoroisocyanate of b. p. 11.5–11.9° at 757 mm., with index of refraction 1.3700 at 2.2°. The actual distillation range of the whole sample indicated that several per cent. of phosphorus trifluoride had been formed. In both cases the purity of the difluoroisocyanate was about 98–99% with a b. p. 12.3 ± 1.0°.

Anal. Calcd. for $PF_2(NCO)$: N, 12.6; mol. wt., 111.0. Found: 12.6; mol. wt., 115.5. No very good method is known for the determination of fluorine in the presence of phosphorous acid.

Physical and Chemical Properties of Fluoroisocyanates and Fluoroisothiocyanate, Table II.—All measurements of properties including vapor pressures of the fluorodiisocyanate and difluoroisothiocyanate were completed within twenty-four hours of final purification; samples were stored meanwhile at −78° to avoid appreciable decomposition. A standardized mercury thermometer, an Abbe refractometer calibrated with water, and a micropycnometer subject to a volume error of one part in five thousand were used. In obtaining the boiling point the fluorodiisocyanate was stirred (by the bulb of a calibrated toluene thermometer) to effect crystallization, which resulted in a sharp m. p. at −55°. Phosphorus difluoroisothiocyanate formed a glass of extraordinary persistence at −180°; vigorous stirring with the pentane thermometer always converted the difluoroisothiocyanate into a crystalline solid of m. p. −108° (cor.), subject to possible uncertainty regarding the nature of the liquid phase.

All the three new compounds are colorless and have unpleasant and irritating odors, while the difluoroisothiocyanate is noticeably a lachrymator. Hydrolysis of the fluorodiisocyanate is comparable to that of phosphorus trichloride in manner and rate. White fumes appear when the difluoroisothiocyanate is exposed to moist air and its hydrolysis proceeds at a moderate rate. In contrast, the hydrolysis of the unfluorinated isocyanate is extremely vigorous.

A mixture of equal volumes of the fluorodiisocyanate and carbon disulfide has a critical solution temperature of approximately −16°, below which two liquid phases appear. With the difluoroisocyanate two phases appear below about 0°. Phosphorus difluoroisothiocyanate and carbon disulfide (50 to 96 volume per cent. the latter) required temperatures below −50° to produce two phases. Hence, solubility decreases in the order: difluoroisothiocyanate, fluorodiisocyanate, difluoroisocyanate.

The lack of a reaction between phosphorus fluorodiisocyanate and sulfur in a sealed tube during twenty hours at 143° indicated an inhibiting effect of fluorine, for the triisocyanate adds sulfur[2] under these conditions. Judging from the boiling point range of the liquid mechanically separated from the sulfur, it contained not less than 99% of fluorodiisocyanate.

Phosphorus Difluoroisothiocyanate

Twenty-seven grams of pure phosphorus triisothiocyanate and 18 g. of antimony trifluoride at 150–200° react at either 100 or 760 mm. pressure to give 6–9 g. of phosphorus difluoroisothiocyanate and essentially no carbon disulfide. However, 110 g. of the black polymeric phosphorus isothiocyanate decomposes at 300° in the presence of 75 g. of antimony trifluoride to yield 24 g. of carbon disulfide and 5 g. of phosphorus difluoroisothiocyanate. Presumably the difluoro compound was formed from the liquid phosphorus isothiocyanate mechanically included in the black polymeric phosphorus isothiocyanate.[6] The polymerization of phosphorus isothiocyanate, whenever it occurred, was accompanied by much swelling and much heat—sources of considerable danger—requiring use of only moderate quantities in a reaction flask not over one-fifth full. The identification of carbon disulfide as a decomposition product was established beyond reasonable doubt: b. p. 46.2–46.3° at 760 mm., index of refraction 1.6227 in white light and density of 1.264, both at 20°; odor same as carbon disulfide, and no test for phosphorus with molybdate.

Experimental.—Three distillations of combined crudes gave material of b. p. 89.7–90.0° at 751 mm., at least 99.9% $PF_2(NCS)$.

Anal. For phosphorus by phosphomolybdate gave 24.0; 24.4 calcd. Found: NCS, 45.2 by silver nitrate–ferric

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[6] Dixon, *J. Chem. Soc.*, **89**, 397 (1906).

ion method; 45.7 calcd. Mol. wt. (Dumas) 160 at 129° and 152 at 190°, indicating more than usual deviation from the ideal gas law; 127 calcd. and 129–135 could be expected.

Discussion

1. The known phosphorus mixed halides now include six stable compounds (difluorochloride,[7] fluorodichloride,[7] fluorodibromide,[7] fluorodiisocyanate, difluoroisothiocyanate, dichloroisocyanate), two less stable ones (chlorodiisocyanate, dichloroisothiocyanate) and two rather unstable compounds (difluorobromide,[7] difluorosiocyanate). In the related silicon series the trifluoroisocyanate is rather unstable, although the trifluorobromide is stable.

2. The existence of phosphorus difluoroisothiocyanate, as the only member of its series, is in agreement with previous preparations. Recalculation of data of Dixon and Taylor[8] by the N^2 formula gives the molar refraction of phosphorus isothiocyanate as 54.52 ml.; this yields (—NCS) = 15.40 ml., clearly in the isothiocyanate range.[9] The value of 25.66 ml. found compares favorably with the value of 25.72 ml. calculated for the difluoroisothiocyanate.

3. Vitrification appears to be rather usual among compounds of this general type,[3] having been noted among: $POCl_2(NCS)$, $PCl_2(NCO)$, $PCl(NCO)_2$, $PF_2(NCS)$ and $SiCl_3(NCS)$—the structural formula of the last is subject to verification.

4. The boiling points of the phosphorus fluoroisocyanates—and also those of the silicon fluoroisocyanates—are an average of 21° higher than those predicted by linear interpolation between the boiling points of the appropriate two binary halides (difluoro-, b. p. −11°; monofluoro-, b. p. 79° expected). An unexpectedly high boiling point of phosphorus difluoroisothiocyanate (90° instead of 21° as calculated) recalls the unexpectedly high boiling points of monohalo silanes, such as the chloride and bromide.

Acknowledgments.—The author thanks Professor George S. Forbes of this Laboratory for helpful suggestions.

Summary

1. Phosphorus isocyanate and antimony trifluoride react without a catalyst yielding both phosphorus fluoroisocyanates; the difluoro member is best prepared from the monofluoro derivative. Phosphorus fluorodiisocyanate, $PF(NCO)_2$, b. p. 98.7°, is quite stable at room temperature. Phosphorus difluoroisocyanate, $PF_2(NCO)$, decomposes rapidly enough at a b. p. of 12° to limit the purification attainable by distillation; this instability is comparable with that of the previously known silicon trifluoroisocyanate and of phosphorus difluorobromide.

2. Phosphorus isothiocyanate and antimony trifluoride yield only one mixed halide, phosphorus difluoroisothiocyanate, $PF_2(NCS)$, b. p. 90.3°, which shows no decomposition in distillation at 760 mm.

Thermal decomposition of black polymeric phosphorus isothiocyanate yields carbon disulfide.

3. Miscibilities of the three new compounds with carbon disulfide have been studied. Several physical properties have been measured.

CAMBRIDGE, MASSACHUSETTS
RECEIVED FEBRUARY 10, 1947

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[7] Booth and Bozarth, THIS JOURNAL, **61**, 2927 (1939); Booth and Frary, *ibid.*, **61**, 2934 (1939).

[8] Dixon and Taylor, *J. Chem. Soc.*, **93**, 2148 (1980).

[9] Delépine, *Ann. chim.*, [8] **25**, 557 (1912).

[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, U. S. BUREAU OF MINES]

X-Ray Diffraction Studies of the Action of Carbon Monoxide on Cobalt-Thoria-Kieselguhr Catalysts. I[1]

BY L. J. E. HOFER[2] AND W. C. PEEBLES[3]

Finely divided cobalt metal and carbon monoxide react to form a product whose composition corresponds to Co_2C.[4] This reaction occurs under conditions of temperature and pressure which do not differ materially from those of the Fischer–Tropsch reaction on cobalt catalysts. Recently this product was found to be a distinct new carbide with a characteristic crystal structure of its own.[5] The carbon in this carbide is very easily converted to methane by the action of hydrogen at 250°, in contrast to the inertness of the carbon formed on cobalt by carbon monoxide at temperatures above 250°. The genesis as well as the characteristics of this carbide suggest that it may be either an intermediate in the Fischer–Tropsch reaction or the crystalline phase whose surface catalyzes the reaction. The chemical and physical behavior of this carbide, especially its formation by carbon monoxide and its destruction by hydrogen, is of fundamental importance to the understanding of the mechanism of the Fischer–Tropsch reaction.

Previous studies of the carburization of cobalt–thoria–kieselguhr catalysts and of the hydrogenation of such carburized catalysts showed that both

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[4] H. Bahr and V. Jessen, *Ber.*, **63**, 2226 (1930).

[5] L. J. E. Hofer and W. C. Peebles, THIS JOURNAL, **69**, 893 (1947).