

[CONTRIBUTION FROM THE ROHM & HAAS COMPANY, REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALABAMA]

Difluorodiazine^{1,2,3}

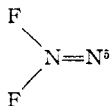
BY CHARLES B. COLBURN, FREDERIC A. JOHNSON, AL KENNEDY, KEITH McCALLUM, LORETTA C. METZGER AND CHARLES O. PARKER

RECEIVED JULY 27, 1959

Difluorodiazine (N₂F₂) has been obtained from the electrolysis of ammonium bifluoride. Difluorodiazine exists as a mixture of *cis* and *trans* isomers which have been separated. Vapor pressure, infrared, mass spectrometric and n.m.r. data are given for each isomer. The *cis* isomer appears to be more reactive than the *trans*. Difluorodiazine catalyzes very markedly certain vinyl polymerizations.

Difluorodiazine (N₂F₂) has been obtained as a minor product [5–10% of the condensable (liquid nitrogen) gases] from the electrolysis of molten (120–130°) ammonium bifluoride. Difluorodiazine was identified by its molecular weight (66) and by its mass spectral cracking pattern. Difluorodiazine was separated from nitrogen trifluoride by a crude fractionation followed either by distillation or vapor phase absorption chromatography on Linde Molecular Sieve 13 X.⁴ Only the *trans* isomer was recovered from this column.

The difluorodiazine obtained from the electrolysis of ammonium bifluoride consisted of a mixture of *cis* and *trans* isomers. The *trans* isomer has been obtained in a purity of 99.7% by chromatography (0.0% *cis*, as established by the absence of *cis* bands in the infrared spectrum). The *cis* isomer has been obtained by low temperature distillation in a minimum purity of 97.5% (maximum 2.1% *trans* isomer, as found by quantitative mass spectral analysis using the mass 66 peak intensity, and assuming no contribution to this peak by the *cis* isomer). There has been fleeting evidence of a possible third very unstable isomer, presumably



The assignment of the *cis* and *trans* isomers was made on the basis of physical properties and infrared absorption. The *trans* configuration has the more symmetrical charge distribution, and is that isomer with the lower boiling point and higher melting point according to the usual rule.⁶ The *cis* isomer possesses a permanent dipole moment and is therefore the higher boiling. The *trans* form⁷ (C₂h) should have three infrared active fundamental bands; one is observed for the lower boiling isomer. The *cis* isomer (C₂v) is expected to have five infra-

red active bands (probably three observed from 1 to 15 microns), and is therefore the other isomer.

TABLE I

Property	PHYSICAL PROPERTIES OF <i>cis</i> AND <i>trans</i> DIFLUORODIAZINE	
	<i>trans</i>	<i>cis</i>
Vapor pressure equation	$\log P_{\text{mm}} = \frac{-742.3}{T} + 7.470$	$\log P_{\text{mm}} = \frac{-803.0}{T} + 7.675$
Boiling point, °C.	-111.4°	-105.7°
Heat of vaporization, cal./mole	3400	3670
Critical temperature, °C.	-13°	-1°
Critical pressure (estimated), atm.	55	70
Melting point, °C.	-172°	Below -195°

The mass spectra (Table II) of the *cis* and *trans* isomers of difluorodiazine were obtained with a Consolidated Model 620 Mass Spectrometer.

TABLE II

MASS SPECTRAL CRACKING PATTERN OF *cis* AND *trans* DIFLUORODIAZINE

M/e	Ion	<i>trans</i> N ₂ F ₂ , %	<i>cis</i> N ₂ F ₂ , %
66	N ₂ F ₂ ⁺	25.3	0.5
47	N ₂ F ⁺	43.4	100.0
33	NF ⁺	5.0	6.0
28	N ₂ ⁺	100.0	84.5
23.5	N ₂ F ⁺⁺	...	1.4
19	F ⁺	1.8	5.3
14	N ⁺	11.6	10.5
Sensitivity of highest peak div./μ		22.36	12.36

The F¹⁹ n.m.r. spectra of the isomers were observed and are given in Table III.

TABLE III

N.M.R. SPECTRA OF *cis* AND *trans* DIFLUORODIAZINE

Compound	δ (cycles from CF ₃ COOH)	J _{N-F} (cycles)
N ₂ F ₂ (<i>cis</i>)	8320	107
N ₂ F ₂ (<i>trans</i>)	6690	53

The infrared spectrum of the *trans* isomer in the rock salt region showed a single p-q-r band centering at 10.05 μ while the *cis* isomer showed much more complex absorption with a strong p-q-r band centering at 10.48 μ and a strong p-r band at 11.07 and 11.33 μ and a very strong p-q-r band centering at 13.57 μ. Also a weak doublet at 6.52 μ and 6.62 μ was observed.

The two isomers of N₂F₂ were found to react differently with glass at room temperature when

(1) Army Ordnance Contract DA-01-021-ORD-5135.

(2) Presented by Charles B. Colburn, at First International Fluorine Symposium, University of Birmingham, Birmingham, England, July 16, 1959.

(3) Personal communication with Professor M. Schmeisser at the Fluorine Symposium revealed that he had done similar work with difluorodiazine. His work (with P. Sartori) was published later as a note in *Angew. Chem.*, **71**, 523 (1959).

(4) Trade mark of Union Carbide and Carbon Corporation, New York, N. Y.

(5) S. H. Bauer, *THIS JOURNAL*, **69**, 3104 (1947).

(6) C. S. Marvel, "Cis-Trans Isomerism" in H. Gilman, "Organic Chemistry," 2nd Ed., Vol. I, John Wiley and Sons, New York, N. Y., 1943, p. 444.

(7) In agreement with R. H. Sanborn, E. O. Lawrence Radiation Laboratory, U. of California, private communication; later presented at symposium on Pure and Applied Spectroscopy, Columbus, 1959.

samples were sealed in capillary tubes for n.m.r. examination. Samples of the *cis* isomer react slowly (completely in two weeks) with the glass with formation of silicon tetrafluoride and nitrous oxide. Samples of the *trans* isomer were essentially unchanged after a month in a sealed glass tube.

It also has been observed that mercury reacts much more rapidly with *cis*-N₂F₂ than it does with the *trans* isomer.

When heated, the *trans* isomer is converted into the *cis* isomer. In glass vessels the isomerization is accompanied by the formation of silicon tetrafluoride and nitrous oxide.

trans-N₂F₂ was found to isomerize in a heated copper tube with little or no side reaction. The isomerization occurred above 225° and as the temperature was increased the rate of the process increased, as expected. Above 300° decomposition to fluorine and nitrogen was extensive. Recoveries of N₂F₂ range from essentially quantitative at the low temperatures to about 60% at 300°. The *cis* isomer predominated at these temperatures.

To establish the existence of an equilibrium mixture of the isomers, mixtures of various compositions were passed through the copper tube at 285° with these results

	Initial % <i>trans</i> N ₂ F ₂	Final % <i>trans</i> N ₂ F ₂
Run I	90.5	13.3
Run II	59.4	12.7
Run III	2.0	13.7

These data obviously represent an equilibrium between the two isomers. An approximate value

for the heat of isomerization is 27.5 ± 5.0 kcal./mole. The activation energy for this isomerization apparently is fairly high since only a small amount (1–2%) of isomerization takes place at room temperature during two weeks time.

An extremely interesting reaction of N₂F₂ is its catalytic effect on polymerization of various monomers. It has been observed that a pressure of 300 mm. of N₂F₂ over these monomers led to their polymerization in twelve hours or less at room temperature: methyl methacrylate, styrene and cyclopentadiene. Difluorodiazine also catalyzed the polymerization of tetrafluoroethylene at 125°. At temperatures in the neighborhood of 140° polymeric substances were formed in the presence of N₂F₂ with ethylene and propylene. These polymers are not, however, polyethylene and polypropylene since they contained fluorine.

Difluorodiazine was first reported by Haller⁸ as arising from the thermal decomposition of fluorine azide. Bauer⁹ reported that electron diffraction of this difluorodiazine indicated a mixture of *cis* and *trans* isomers.

Caution should be used in working with difluorodiazine in the presence of organic material and it never should be condensed into or onto organic material, as the danger of explosion is great. Mercury manometers should be protected with Kel-F⁹ oils and hydrocarbon and silicon stopcock greases should be avoided in favor of Kel-F⁹ stopcock grease.

(8) J. F. Haller, Ph.D. Thesis, Cornell University, 1942.

(9) Trade mark of Minnesota Mining and Manufacturing Co., Minneapolis, Minnesota.

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

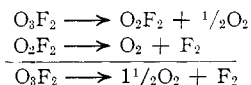
The Heat of Formation of O₂F₂ and O₃F₂^{1,2}

BY A. D. KIRSHENBAUM, A. V. GROSSE AND J. G. ASTON³

RECEIVED JUNE 4, 1959

A method has been developed for determining heats of formation of substances that decompose spontaneously below 0°. The heats of decomposition of liquid O₂F₂ and liquid O₃F₂ into gaseous oxygen and fluorine have been determined directly at temperatures of 190 and 121°K., respectively, by this method. From these values the heats of formation of the gaseous compounds at 298°K. have been calculated along with the relevant bond energies. A comparison of these bond energies with values in other compounds indicates considerable resonance stabilization. The heats of formation, $\Delta H_{298^\circ\text{K}}$, for O₂F₂ and O₃F₂ are $+4.73 \pm 0.30$ and $+6.24 \pm 0.75$ kcal./mole, respectively. The $\Delta H_{121^\circ\text{K}}$ of the reaction $\text{O}_3\text{F}_2(1) \rightarrow \text{O}_2\text{F}_2(1) + \frac{1}{2}\text{O}_2(\text{g}) = -1.91 \pm 0.15$ kcal./mole.

O₂F₂ has been known for some time⁴ but proof of the existence of O₃F₂, its preparation and chemical and physical properties have only recently been reported.⁵ O₂F₂ and O₃F₂ are stable below 195 and 120°K., respectively. At higher temperatures, however, O₂F₂ decomposes into O₂ + F₂ while O₃F₂ decomposes stepwise as



This paper presents values of the heat of formation of O₂F₂ and O₃F₂ obtained by direct measurement of the heat of decomposition of the compounds into the elements.

Choice of Method.—In these studies it has been possible to use apparatus of an almost conventional sort by merely adapting the room temperature submarine calorimeter^{6–8} for operation at rela-

(1) Presented before the Physical Chemical Division at the Boston ACS Meeting, April 7, 1959.

(2) This work was financed by the Army Ballistic Missile Agency, Redstone Arsenal, Huntsville, Alabama.

(3) Dept. of Chemistry, The Pennsylvania State University, Consultant to the Research Institute.

(4) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **211**, 204 (1933).

(5) A. D. Kirshenbaum and A. V. Grosse, *THIS JOURNAL*, **81**, 1277 (1959).

(6) W. F. Giaque and R. C. Archibald, *ibid.*, **59**, 561 (1937) (see Fig. 4 of their paper).

(7) J. G. Aston and C. W. Ziemer, *ibid.*, **68**, 1405 (1946).

(8) F. T. Gucker, Jr., F. D. Ayres and T. R. Rubin, *ibid.*, **58**, 2118 (1936).