

On the Molecular Configuration of Cyclic C₄F₈

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given values of from 2° to 5° and with $\theta = 25^\circ$ give rise to acceptable intensity curves. A typical model has bonded C—F distances ranging from 1.31 to 1.35 Å, the bonded C—C distances about 0.02 Å less than the frequently observed values of 1.34 and 1.54 Å, the FCF angles nearly tetrahedral, $\angle C_1C_2C_3 = 126^\circ$ and $\angle C_1C_2F_2 = 114^\circ$.

Because of the large number of parameters it is not possible to eliminate all "planar" models but in view of the failure to find an acceptable "planar" model after many trials, the authors believe that the structure of this compound is best represented by a "strained" model in which none of the fluorine atoms is in the plane determined by the three carbon atoms. The strains are attributed to repulsions between fluorine atoms which are attached to different carbon atoms; these repulsions apparently twist the double bond to such an extent that the closest approach of fluorine atoms is almost exactly twice the van der Waals radius of fluorine, i.e., 2×1.35 Å. Additional and somewhat more conclusive evidence for the importance of such strains has been found in the halogenated benzenes² and in C_4F_8 .³

* From the Ph.D. thesis of F. A. M. Buck, du Pont Fellow in Chemistry, Purdue University, 1947–48.

¹ F. A. M. Buck and R. L. Livingston, *J. Am. Chem. Soc.* **70**, 2817 (1948).

² O. Bastiansen and O. Hassel, *Acta Chemica Scandinavica* **1**, 489 (1947).

³ H. P. Lemaire and R. L. Livingston, *J. Chem. Phys.* **18**, 569 (1950).

On the Molecular Configuration of Cyclic C_4F_8

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December 8, 1949

SEVERAL years ago one of us² studied the Raman spectrum of perfluorocyclobutane and concluded that it and the data then available on the infra-red spectrum "are in harmony with the planar ring model of symmetry D_{4h} ." The spectra have been investigated again with better equipment and new data obtained.

The sample used in this work was prepared by the pyrolysis of teflon.³ Experimental details will be presented later. The Raman spectrum was determined in the liquid state at about $-25^\circ C$ using a Lane-Wells spectrograph of camera aperture $F/3$. The results are found in Table I. Lines were also found shifted 301,

TABLE I. The Raman spectrum of cyclic C_4F_8 (to 1450 cm^{-1}).

$\omega\text{ (cm}^{-1}\text{)}$	Density*	$\omega\text{ (cm}^{-1}\text{)}$	Density*
190	m	783	vw
256	s	857	vw
272	s	971	w
346	m+	1008	s
361	vs	1052	w
440	vs	1216	s
573	vw	1278	m+
605	w+	1340	w
659	m	1398	vw
699	vs		
722	m	1431	m+

* s = strong, m = medium, w = weak, v = very.

382, 598, 643, 906, and 954 cm^{-1} from the Hg 4358 Å exciting line. These are believed to be the fundamentals 361, 440, 699, and 1008 cm^{-1} excited by Hg 4348 or Hg 4339 Å.

The infra-red spectrum was obtained with a Perkin-Elmer spectrometer, Model 12B, using NaCl and KBr optics. The results, through the region of the fundamentals, are found in Table II. Relative intensities are based on the scale: vs, 50 percent absorption at 2.5 mm pressure; s, 50 percent at 12.5 mm; m, 50 percent at 500 mm; w, 50–25 percent at 500 mm; vw, <25 percent at 500 mm, all in a 10-cm cell.

In general, the data obtained in another recent study of this molecule⁴ are in good agreement with those presented here. They have been interpreted in terms of the planar ring model.

TABLE II. The infra-red spectrum of cyclic C_4F_8 (400 to 1450 cm^{-1}).

$\omega\text{ (cm}^{-1}\text{)}$	Intensity*	$\omega\text{ (cm}^{-1}\text{)}$	Intensity*
425	vw	864†	w
444	m	890	w
467	w	899	w
502	vw	962	vs
531	vw	981	m
571	vs	1002	m
606	vw	1093	m
632	vw	1120	w
659	w	1153	s
684	w	1224†	vs
729†	w	1239†	vs
731†	w	1268	m
799	vw	1290	vs
845†	w	1229	vs
851†	w	1394	s
858†	w	1448	w

* s = strong, m = medium, w = weak, v = very.

† Peaks in a "single band" or region of absorption.

If cyclic C_4F_8 has a planar ring structure of symmetry D_{4h} , eleven fundamentals would be Raman active. Almost twice this number of lines are found in the spectrum range of the fundamentals, fifteen of which are of sufficient intensity to appear on all films of reasonable exposure. A molecule with this point group has a center of symmetry and transitions permitted in the Raman spectrum are forbidden in the infra-red spectrum and vice-versa. More than half of the Raman lines in the region of common observation correspond to infra-red bands with almost exact numerical coincidence or within the limits to be expected of spectra taken in different phases.

With the D_{4h} model, these features of the spectra must be attributed to the breakdown of selection rules either in the liquid state or at higher pressures, near coincidences in the frequencies of similar fundamental modes of vibration and the appearance of overtones or combinations in the Raman spectra. Because of the number of the "discrepancies" and the fact that allowed fundamentals of highly fluorinated molecules often appear weakly in Raman and infra-red spectra, it is believed that a question should be raised as to the correctness of the D_{4h} model. Independent evidence is required to prove this point.

An electron diffraction study of this molecule has been carried out by Lemaire and Livingston.⁵ They were unable to interpret their results in terms of the planar ring model of symmetry D_{4h} . Agreement between calculated and observed patterns were obtained for a model of symmetry V_d , the most likely non-planar ring structure.

One of us (W. F. E.) wishes to express his gratitude to the Research Corporation for a grant which made the purchase of the Lane-Wells spectrograph possible. Thanks are also due Mr. H. D. Mallory for preparing several Raman spectrograms and the Central Research Laboratories, Minnesota Mining and Manufacturing Company, for the samples.

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² Walter F. Edgell, *J. Am. Chem. Soc.* **69**, 660 (1947).

³ E. Lewis and M. Naylor, *J. Am. Chem. Soc.* **69**, 1968 (1949).

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The Mechanism of the Decomposition of N_2O on ZnO as Catalyst

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February 3, 1950

UNDER this heading, Wagner¹ reports an attempt to correlate catalytic activity with conductive properties. Observing that the conductivity of $ZnO + 1\text{ percent } Ga_2O_3$ is 50 times greater than that of ZnO but that the rate of N_2O decomposition on these catalysts differs by a factor less than two, he concludes that the

"... attempt to develop a mixed catalyst with an outstanding activity has been a failure." This failure however is not due to an absence of correlation between activated adsorption and conductive characteristics of the adsorbent but to a deceptive choice of the operative parameter. Volkenshtein² has shown that the main features of activated adsorption (activation energy, isotherms, differential adsorption heats decreasing with coverage) can be obtained with an energetically homogeneous but temperature sensitive surface. Active centers may be originally present but new ones are produced either on filling up at constant temperature or by a temperature increase, at the expense of an energy E which appears as an activation energy in the rate equation for adsorption. In certain cases, we may identify E with the energy ϵ necessary to send a bound electron into the conduction band. Details will be described elsewhere. Let it be said only that such an activation throws much light on some facts which were obscure from the standpoint of the usual theories. Since 1932, Taylor³ has repeatedly emphasized that the observed adsorption rates were not compatible with the assumption that every molecule hitting the surface with the necessary activation energy is adsorbed. Pace and Taylor,⁴ reporting that the adsorption rates for H_2 and D_2 on Cr_2O_3 and $ZnO-Cr_2O_3$ are identical, suggested that "the activation energy of the adsorption process is required by the solid adsorbent." This activation of the solid has also been considered by Hedvall⁵ whose concepts have been examined by Möglich.⁶

Assuming that the concentration of quasi-free electrons is rate determining, Wagner concludes that 1 percent Ga_2O_3 has no influence on the reaction velocity and he defines active centers of a special nature. No such restrictive hypothesis is needed if absolute values of K (specific conductivity) are of little interest but if ϵ has to be measured and appreciated as the determining parameter. There is a relationship between K and ϵ (Meyer's "straight line") but from the data which led Meyer to his systematization and from their analysis by Gisolf,⁷ it can be seen that large differences in conductivities do not entail a large difference $\Delta\epsilon$ between the corresponding values of ϵ ; $\Delta\epsilon$ actually depends on changes in concentrations of both defects and electron traps and can be quite small. If it were 1350 cal. mole⁻¹, the reaction rates would differ at 725°C by a factor of two only.

We thus think that Wagner underestimated the scope of his own work. Further attempts to correlate adsorption and catalysis with semiconductivity ought to include measurements of both K and ϵ .⁸ We wish to express our indebtedness to Professor H. S. Taylor who suggested a large number of the ideas contained in this note.

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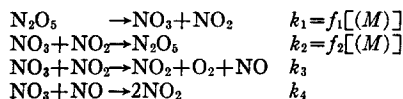
Quasi-Unimolecular and Quasi-Bimolecular Steps in Complex Reactions. The Dissociation of Nitrogen Pentoxide

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February 15, 1950

THE mechanism previously proposed¹ for the decomposition of N_2O_5 entails a hitherto unemphasized prediction of an apparent "falling off" of the first-order rate constant at *extreme low pressure*. In the reformulation below, the symbol M denotes the molecular species responsible for collisional activation and deactivation.



(The rate constant for step 4, not comprised in the original formulation, does not appear in the rate expression for the decomposition. It is required to explain the kinetics of the reaction between N_2O_5 and added NO.) The various detailed theories² of quasi-unimolecular reactions allow derivation (on the basis of assumed molecular models) of specific mathematical forms for the function f_1 . Inasmuch as k_1/k_2 is an equilibrium constant, f_1 and f_2 are identical in form, in the sense that $f_1[(M)_A]/f_1[(M)_B] = f_2[(M)_A]/f_2[(M)_B]$. The various theories converge in the region of extreme low pressure—i.e., as $(M) \rightarrow 0$, $k_1 \rightarrow k_{act}(M)$, where k_{act} is the collisional activation constant.

The following rate expression results for the decomposition.

$$-\frac{d(N_2O_5)}{dt} = k_{ex}(N_2O_5) = \frac{2k_1k_3}{k_2 + 2k_3}(N_2O_5).$$

As previously shown, when $(M) \rightarrow \infty$, $k_2 \gg 2k_3$ and hence

$$k_{ex, \infty} = \frac{2k_1k_3}{k_2}.$$

At all values of (M)

$$\frac{1}{k_{ex}} = \frac{k_2}{2k_1k_3} + \frac{1}{k_1} = \frac{1}{k_{ex, \infty}} + \frac{1}{k_1}.$$

As $(M) \rightarrow 0$, $k_1 \rightarrow k_{act}(M)$,

$$\frac{1}{k_{ex, 0}} \rightarrow \frac{1}{k_{ex, \infty}} + \frac{1}{k_{act}(M)}.$$

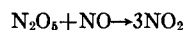
The above conclusion as to eventual falling off of k_{ex} is strikingly confirmed by the studies of Linhorst and Hodges³ performed at pressures of the order of 10^{-3} mm Hg. Their empirical equation is of exactly the above linear form. From their data at various temperatures, for M simply N_2O_5 itself, the collisional activation rate constant

$$k_{act} = 10^{18.9} e^{-\frac{18,300}{RT}} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}.$$

The activation energy of step 1 at high pressures cannot be less in absolute value than the energy change associated with this process. From the previous estimate¹ a value of about 21.6 kcal./mole seems very probable for this activation energy. It is seen above that the limiting value at extreme low pressures is some 18.3 kcal./mole. In the Kassel² classical model based theory, this difference is merely $(s-3/2)RT$, where s is the effective number of classical oscillators. Noting that these figures apply to some 300°K, the corresponding value for s is about 7. This is entirely reasonable in view of the maximum possible value of 15 for N_2O_5 . Using $s=7$, the above frequency factor leads to a collisional deactivation rate constant of some 10^{16} mole⁻¹ cm³ sec⁻¹. The collision diameter corresponding to this figure is in sensible agreement with the viscosity studies on N_2O_5 .⁴

The above estimated activation energy and a "normal" frequency factor lead to an expected limiting high pressure value of k_1 at 300°K of the order of magnitude of 10^{-1} sec⁻¹. From the above estimate of s the classical theory of Kassel² predicts that N_2O_5 pressures of the order of hundreds of millimeters of Hg would be necessary to reach *one-half* of the limiting high pressure value of k_1 . Thus step 1, when studied separately, is expected to show very marked falling off of rate constant at moderate pressures, and should be markedly accelerated by addition of chemically indifferent gases.

The work of Smith and Daniels⁵ on the kinetics of the reaction



offers one approach to study of the rate of step 1. Neglecting step 3 the resulting rate expression is

$$-\frac{d(NO)}{dt} = \frac{k_1(N_2O_5)}{1 + [k_2(NO_2)/k_4(NO)]}.$$

The reaction was observed to be zero order with respect to NO, but no marked inhibitory effect of NO_2 was found. At the relatively very low pressures used, the value of k_2 has apparently