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Molecular Association in Hydrogen Fluoride Vapor

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 March 24, 1947

DENSITY measurements¹⁻⁴ of hydrogen fluoride vapor have shown the existence of strong molecular association in a region of temperature and pressure extending some distance above the boiling point. Simons and Hildebrand² and Long, Hildebrand, and Morrell⁴ were able to calculate the densities on the assumption of the existence of a single equilibrium $6\text{HF} \rightleftharpoons (\text{HF})_6$, although some indication of the formation of lower polymers at low degrees of association was also obtained. Briegleb,⁵ on the other hand, concluded that the association was of the type, $\text{HF} + (\text{HF})_n \rightleftharpoons (\text{HF})_{n+1}$, and calculated from the data of Fredenhagen³ values of the equilibrium constants for the cases $n = 1, 2, \dots, 8$. Hildebrand and his co-workers considered the hexamer to be stabilized by linking of the two ends of the chain to form a hexagonal ring, and Pauling⁶ calculated that the additional bond obtained by ring formation would make a ring containing six or more hydrogen fluorides more stable than its chain analog. Electron diffraction measurements⁷ indicated that the molecules were zig-zag chains of different lengths, mostly trimers, tetramers, and pentamers. However, it was recognized that there was a slight possibility that ring structures might have dissociated into chains during the course of the measurements, which were made as a molecular beam passed into a vacuum.

Dielectric constant measurements⁸ in a region of temperature and pressure where molecular association was negligible gave a dipole moment 1.91×10^{-18} for the monomeric hydrogen fluoride molecule. A polymeric molecule in the form of a plane ring or a puckered ring with the fluorines at the corners and the hydrogens in the edges would have zero dipole moment. An extended rectilinear chain or an extended zig-zag chain with the hydrogens in the fluorine-fluorine lines, as indicated by electron diffraction, would have a larger moment than the monomer. Measurement of the dielectric constant of the vapor and calculation of its polarization, P , which, for hydrogen fluoride with its very small molar refraction is approximately proportional to the square of the dipole moment, can thus give evidence of the presence or absence of any considerable amount of ring formation.

The apparatus previously used⁸ in the determination of the hydrogen fluoride dipole moment was employed after slight alterations. The insertion of a second nickel reservoir and an additional Bourdon gauge facilitated the purification of the hydrogen fluoride by fractional distillation. The purity of the carefully purified sample used in the measurements was checked by determination of its liquid vapor pressure. As the effect of the deviation from the ideal gas law for each kind of molecule was insignificant in comparison with the effect of the molecular association, the polarization, P , was calculated from the dielectric constant, ϵ , by means of the simple equation

$$P = RT(\epsilon - 1)/p(\epsilon + 2),$$

in which R is the gas constant, T , the absolute temperature, and p , the pressure.

Two curves were run for polarization as a function of pressure, one at 26.0° and the other at 38°C, temperatures at which the association had been established by previous investigations.⁴ At both temperatures, the polarization values at pressures below 100 mm showed no measurable variation with change of pressure, in agreement with the indications given by the density measurements.⁴ These polarization values were consistent with those previously found by Hannay and Smyth.⁸ For pressures above 120 mm at 26.0° and 160 mm at 38.0°, the polarization rose rapidly with increasing pressure, the rise being more rapid at the lower temperature and continuing with increasing pressure up to the highest pressures observed, 551 mm at 26.0° and 707 mm at 38°. The large increase in polarization brought about by molecular association shows that ring structures, which would decrease the polarization, cannot predominate and the presence of more or less extended chains, which, because of their large dipole moments, increase the polarization, is clearly indicated.

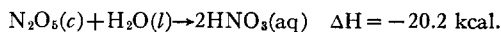
A detailed discussion of the quantitative data will be given when the measurements now being carried out in this laboratory are completed.

- ¹ T. E. Thorpe and F. J. Hambly, *J. Chem. Soc.* **55**, 163 (1889).
- ² J. Simons and J. H. Hildebrand, *J. Am. Chem. Soc.* **46**, 2183 (1924).
- ³ K. Fredenhagen, *Zeits. f. anorg. allgem. Chemie* **218**, 161 (1934).
- ⁴ R. W. Long, J. H. Hildebrand, and W. E. Morrell, *J. Am. Chem. Soc.* **65**, 182 (1943).
- ⁵ G. Briegleb, *Zeits. f. physik. Chemie* **51B**, 9 (1941).
- ⁶ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), p. 298.
- ⁷ S. H. Bauer, J. Y. Beach, and J. H. Simons, *J. Am. Chem. Soc.* **61**, 19 (1939).
- ⁸ N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.* **68**, 171 (1946).

The Mechanism of Nitrogen Pentoxide Decomposition

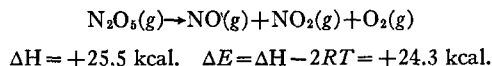
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 April 15, 1947

CONSIDERATIONS of reaction mechanism discussed below suggested a probable serious error in the previously accepted value for the heat of formation of nitrogen pentoxide. Accordingly, the heat of solution of this substance in water has been redetermined. Extremely pure samples were obtained by resubliming in a stream of ozonized oxygen the product from nitric acid-phosphorus pentoxide reaction. The calorimetric procedure amounted to direct comparison of the desired heat of solution with the heat of neutralization of dilute aqueous nitric acid and sodium hydroxide. The results of four duplicate determinations (respective values 20.0, 20.8, 20.2, and 19.8 kilocalories) give as an average value (at 25°C)

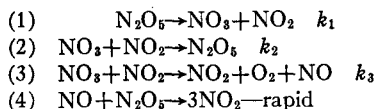


The considerably smaller value of 16.7 kcal. found by Berthelot¹ is scarcely surprising in view of the difficulties in purification of this notoriously reactive and unstable substance. Using the above new value, and other requisite thermochemical data² of relatively modern origin, one finds

the heat of formation of $\text{N}_2\text{O}_5(c)$ to be 9.6 kcal. per mole, and for the following reaction (at 25°C)



It is proposed that the apparently first-order decomposition of N_2O_5 is in reality a chemically complex process involving the transient intermediate NO_3 —a well-recognized substance which plays an important role in related reactions.³ Steps of the suggested mechanism follow, with indicated rate constants.



The rate constant k_2 would be expected to be similar in magnitude to that for the corresponding recombination of NO_2 radicals—known to have at most a very small activation energy.³ However, it will appear that reaction (3) is endothermic, and hence has appreciable activation energy. Consequently, at relatively low temperatures ($\sim 25^\circ\text{C}$), $k_3 \ll k_2$. By the usual "steady-state" treatment one finds

$$-\frac{d(\text{N}_2\text{O}_5)}{dt} = 2\frac{d(\text{NO})}{dt} = 2\frac{k_1 k_3}{k_2 + k_3} (\text{N}_2\text{O}_5) \sim 2\frac{k_1}{k_2} k_3 (\text{N}_2\text{O}_5).$$

The apparent first-order rate constant is thus in reality the product of an *equilibrium* constant (k_1/k_2) and a *second-order* rate constant (k_3). Hence no "falling off" of constants at low pressures is to be expected. The exhaustive experimental tests³ have shown this to be the case—a fact for which no reasonable explanation could be offered on the basis of the collisional activation theory of first-order reactions.

The proposed quasi-equilibrium dissociation of N_2O_5 is supported by the observations of Ramsperger and Tolman⁴ that at extremely low concentrations the ratio of final to initial pressures falls considerably *below* the value 2.5 corresponding to the reaction $\text{N}_2\text{O}_5 \rightarrow 2\text{NO}_2 + \frac{1}{2}\text{O}_2$. The data of these authors allow one to estimate rough values of the equilibrium constants for the dissociation $\text{N}_2\text{O}_5 \rightleftharpoons \text{NO}_3 + \text{NO}_2$. If the corresponding entropy change is assumed to be similar to those for N_2O_4 and N_2O_3 dissociation, the dissociation energy is estimated very approximately as some 18–22 kcal. per mole (compare 14.0 and 9.7 for N_2O_4 and N_2O_3 , respectively⁵).

The revised thermochemical values supply the strongest support of the proposed mechanism. Denoting reaction energies as " E ," activation energies as " Q ," and experimental values by the subscript " Ex ," since

$$k_{Ex} = 2(k_1/k_2)k_3, \quad Q_{Ex} = E_1 + Q_3.$$

However, if (3) is endothermic by amount E_3 , $Q_3 \geq E_3$ and hence $Q_{Ex} \geq E_1 + E_3$. Adding (1) and (3) and applying Hess' Law



From the above new data, $E_1 + E_3 = 24.3$ kcal.—as compared with $Q_{Ex} = 24.6$ kcal. The near identity of these values suggests that Q_3 exceeds E_3 by very little. If E_1 is

taken roughly as ~ 20 kcal., Q_3 is thus ~ 5 kcal.—a value sufficient to ensure the inequality $k_3 \ll k_2$.

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³ L. S. Kassel, *Kinetics of Homogeneous Gas Reactions* (Chemical Catalogue Company, New York, 1932).

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The Detection of Radioactive Persulfate Fragments in Emulsion Polymerized Styrene

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February 4, 1947

PRICE and co-workers¹ have shown that fragments of organic peroxide catalysts are chemically combined with polystyrene polymerized in oil phase. It is a much more difficult problem to demonstrate by chemical analysis the presence in the polymer of fragments of the inorganic peroxides normally used as catalysts in emulsion polymerization because of the high molecular weights of the polymers produced in emulsion in the absence of chain transfer agents. However, by the use of potassium persulfate prepared from radioactive S^{35} it has now been found that fragments (containing sulfur) of the potassium persulfate used as a catalyst in the emulsion polymerization of styrene are chemically combined with the polystyrene.

Radioactive potassium persulfate was prepared by electrolysis of potassium sulfate in sulfuric acid containing radioactive S^{35} . The radioactive S^{35} was received as a trace constituent of potassium chloride supplied by the Clinton Laboratories of the Monsanto Chemical Company.

The active potassium persulfate was used as a catalyst in polymerizing styrene in a soap emulsion. The polystyrene produced was purified by precipitating it from the emulsion with methyl alcohol, then dissolving in benzene and reprecipitating with methyl alcohol, the dissolving and reprecipitating being done three successive times. The polystyrene was then examined for radioactivity with a Geiger counter of the end window type.²

The background count was 2.5 counts per sec. A 0.1-mg sample of the potassium persulfate dried from solution in an aluminum dish gave a count of 480 sec.⁻¹. A sample of 50 mg of the purified polystyrene gave a count of 65.9 sec.⁻¹. An additional purification of the polystyrene by precipitating from benzene with methyl alcohol left the activity substantially unchanged, i.e., the count obtained was 65.3 sec.⁻¹.

Thus, sulfur containing fragments of the persulfate must be chemically combined with the polystyrene. We are now endeavoring to obtain the quantitative relation between persulfate fragments and number of polymer molecules.

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