



Fig. 1.—Log k_{obs} vs. $-H_0$ for the hydrolysis of 4-dimethoxymethylpyridinium ion in perchloric acid at 25°

$\log(f_M f_{\text{BH}^+}/f_{\text{tr}^+} f_{\text{B}})$, more specifically to salt effects on f_M , the activity coefficient of neutral methylal, and f_B , that of the indicator base used to measure H_0 .^{4,5} The similarity between the slopes for methylal and 4-dimethoxymethylpyridinium ion hydrolyses implies that $d \log(f_{\text{SH}^+}/f_{\text{tr}^+})/dH_0 \cong d \log(f_M/f_{\text{tr}^+})/dH_0$. This is provided, of course, that $d \log(f_B/f_{\text{BH}^+})/dH_0$ is the same for the indicator bases used to measure the H_0 values in the two instances.²³

The value of ΔH^\ddagger in 43.35% perchloric acid, determined from rate constants at three temperatures

(23) That $d \log(f_B/f_{\text{BH}^+})/dH_0$ be the same for all indicator bases is, of course, basic to the entire Hammett scale. However, this can be experimentally verified only for "adjoining" indicator bases over a narrow region of overlap of mineral acid concentrations.^{14,15} Whether it remains true for the indicator bases used between 4 and 35% perchloric acid (acid region used for methylal hydrolysis) as compared to those used between 36 and 50% perchloric acid (acid region used for 4-dimethoxymethylpyridinium ion hydrolysis), is a moot question.¹⁵

(Table I), is 22.6 ± 0.2 kcal./mole, and ΔS^\ddagger at 25° is $+4.5 \pm 0.6$ e.u. The positive entropy of activation is within the range considered normal for one-proton hydrolysis reactions proceeding via an A-1, *i.e.*, Hammett unimolecular, mechanism.¹⁵

The w -Value.—Bunnett has recently proposed that the value of the parameter w , defined as the slope of the plot of $\log k_{\text{obs}} + H_0$ vs. $\log a_{\text{H}_2\text{O}}$, be used in the precise classification of acid-catalyzed reactions.²⁴ For reactions which presumably follow the Hammett mechanism, *i.e.*, rate-controlling unimolecular decomposition of substrate conjugate acid, w lies in the range zero to -2 .^{24c} For the hydrolysis of 4-dimethoxymethylpyridinium ion in 36–50% perchloric acid the w -value is -0.34 ± 0.02 , whereas for methylal hydrolysis in 4–35% perchloric acid it is -2.04 ± 0.19 .^{24b} This difference in the w -value for two presumably mechanistically identical reactions can be rationalized in the terms used by Bunnett, namely that the w -value equals "hydration of transition state less substrate on a scale set by the 'water balance' in protonation of an indicator base."^{24d} That is, one could invoke a solvation-saturation phenomenon in arguing that the increase in solvation hydration in going from a positively charged substrate to a doubly positive transition state is less than in going from a neutral substrate to a transition state having one positive charge.

Our results are pertinent to the problems of the mechanism of hydrolysis of nicotinamide, isonicotinamide and picolinamide.²⁵ Bunnett has pointed out that hydrolysis of these pyridinium amides has a considerably higher w -value than that of other, neutral, amides and has suggested that this may be due either to the presence of the positive charge on the substrate or to the incursion of another mechanism.^{24e} The relative similarity between the w -values for the hydrolysis of methylal and 4-dimethoxymethylpyridinium ion strongly suggests that the latter explanation is the correct one.

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(24) (a) J. F. Bunnett, *J. Am. Chem. Soc.*, **82**, 499 (1960); (b) **83**, 4956 (1961); (c) **83**, 4968 (1961); (d) **83**, 4973 (1961); (e) **83**, 4978 (1961).

(25) (a) H. H. G. Jellinek and A. Gordon, *J. Phys. Chem.*, **53**, 996 (1949); (b) H. H. G. Jellinek and J. R. Urwin, *ibid.*, **57**, 900 (1953).

COMMUNICATIONS TO THE EDITOR

XENON HEXAFLUORIDE¹

Sir:

The preparations of XeF_4^2 and $\text{XeF}_2^{3,4}$ have been reported. We have found that at high excess fluorine pressures a more volatile compound is formed. Chemical and radiochemical analyses show this to be xenon hexafluoride, XeF_6 .

In a typical preparation 5.25 millimoles of xenon and 110 millimoles of fluorine were heated for 16 hours at

300° in a nickel reaction vessel. The pressure in the vessel was calculated to be about 60 atmospheres at 300°. After the reaction the vessel was allowed to cool to room temperature, immersed in a -78° bath, and the excess fluorine pumped off. The volatile product was purified by sublimation into a trap at -78° . A number of preparations have been carried out under similar conditions and yields of XeF_6 of greater than 90% have been obtained.

The formula of the compound has been established as XeF_6 by a method described previously.² The hexafluoride was reduced with hydrogen and the xenon and hydrogen fluoride produced were collected and weighed. Results: (1) XeF_6 taken, 0.3934 g.; Xe found 0.2125 g., calculated 0.2106 g.; F found 0.1770 g., calculated

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(3) J. L. Weeks, C. L. Chernick and M. S. Matheson, *ibid.*, in press.

(4) D. F. Smith, *J. Chem. Phys.*, in press.

0.1828 g.; F/Xe = 5.79. (2) XeF₆ taken, 0.2256 g.; Xe found 0.1195 g., calculated 0.1208 g.; F found, 0.0996 g., calculated 0.1048 g.; F/Xe = 5.76.

The radiochemical work was done in a similar manner but using smaller amounts, about 0.07 millimole of xenon and 4 millimoles of fluorine, and heating for only one hour. The final pressure in the reaction vessel was about 50 atmospheres. Xe¹³³ and F¹⁸ were used as tracers to measure the combining ratios of xenon and fluorine. The reaction vessel could be placed in the well of a sodium iodide scintillation crystal which fed a single channel analyzer. The counting technique is more fully described elsewhere.⁵ The specific activities of the xenon and fluorine were measured initially and in the product after heating. In two experiments at 300° and two at 400° the fluorine to xenon ratios obtained were 5.8, 5.9, 5.8 and 5.8.

Mass spectrographic analyses of purified samples showed the presence of XeF₆⁺ and its fragmentation products.

Xenon hexafluoride is a colorless solid, with a vapor pressure of about 7.5 mm. at 0° and 30 mm. at 25°. In a polychlorotrifluoroethylene tube it was observed to turn yellow at about 42° and melt to a yellow liquid at 46°. On solidifying it was again colorless. The vapor has a pale yellow color.

The compound is stable at room temperature and has been stored for weeks in a nickel can without decomposition. Samples sealed in quartz cells appear to react slowly to produce a clear, colorless liquid.

Xenon hexafluoride reacts violently with hydrogen or water at room temperature. It dissolves without reaction in anhydrous hydrogen fluoride.

A preliminary scan of the infrared spectrum of the vapor has been made from 4000 to 400 cm.⁻¹. Only one strong infrared band at 612 cm.⁻¹ was found. This frequency is in the region where ν_3 has been observed for hexafluorides with bond lengths of about 2 Å., e.g., UF₆.⁶

The spectral region from 26,000 to 1900 Å. has been investigated for XeF₆ vapor, revealing an intense absorption maximum at 3300 Å. some 500 Å. wide at half-height and a still more intense absorption at wave lengths shorter than 2750 Å.

(5) I. Sheft, H. H. Hyman, R. M. Adams and J. J. Katz, *J. Am. Chem. Soc.*, **83**, 291 (1961).

(6) H. H. Claassen, *J. Chem. Phys.*, **30**, 968 (1959).

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XENON HEXAFLUORIDE

Sir:

Recently, Claassen, Selig, and Malm reported the direct fluorination of Xe vapor at 400° to form XeF₄ and an unidentified lower xenon fluoride,¹ which subsequently was identified as XeF₂.^{2,3} No indication of the existence of a higher fluoride than XeF₄ has been reported. This communication reports the preparation of XeF₆ and some of the properties of this compound.

The reactor used in the preparations was a cylindrical high pressure stainless steel vessel of 250 ml. volume provided with an internal electric heater made with nickel gauze. All of the reactions were carried out at an initial total pressure of 1000 p.s.i. The ratio of

(1) H. H. Claassen, H. Selig, and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(2) C. L. Chernick, *et al.*, *Science*, **138**, 136 (1962).

(3) D. F. Smith, *J. Chem. Phys.*, in press.

fluorine to xenon was varied from 6 to 40. Filament temperatures in the range 350–450° were used. The walls of the reactor were either maintained at about -115° or at 80°. In all cases a mixture of volatile products was obtained. These were partially separated by a series of bulb-to-bulb distillations using a variety of reservoirs and collecting temperatures below 0°. The more volatile fractions always concentrated XeF₆. The less volatile fractions concentrated XeF₂, XeF₄, and an unidentified xenon fluoride of comparable volatility.

The purity of the samples was monitored by infrared spectroscopy. The identifying feature of XeF₆ is a strong fundamental at 610 cm.⁻¹, presumably ν_3 . Three other strong absorptions were observed in the KBr range, with the impure samples: ν_3 of XeF₂ at 550 and 566 cm.⁻¹,³ the stretching frequency of XeF₄ at 582 and 592 cm.⁻¹,^{1,2} and a broad band at 520 cm.⁻¹ not associated with any of the xenon fluorides mentioned above. In the highest purity sample of XeF₆ obtained thus far, all of the three above bands were absent. In the purest XeF₆ sample, the twin bands, $\nu_2 + \nu_3$ and $\nu_1 + \nu_3$, characteristic of all the other hexafluorides, were observed at 1154 and 1189 cm.⁻¹. The details of the infrared spectra of XeF₆ obtained to date are consistent with a symmetrical structure for the molecule. If the band at 1189 cm.⁻¹ is $\nu_1 + \nu_3$, then ν_1 is 579 cm.⁻¹. This is the lowest value for the totally symmetrical vibrational frequency, ν_1 , observed for the sixteen known hexafluoride molecules and suggests that XeF₆ is the least stable hexafluoride. This latter statement is also consistent with our qualitative chemical observations.

The formula for XeF₆ was established by chemical analysis. Samples of XeF₆ were distilled into a nickel weighing vessel containing mercury and the weight of sample determined from the weight increase. The reaction between XeF₆ and Hg was carried out at 100° and the Xe produced subsequently distilled out of the cooled weighing vessel. The procedure was continued until no further loss in weight of the container was observed. The increase in weight of the container over its initial weight gave the fluorine content of the sample; the xenon content was calculated by subtracting the weight of fluorine from the total weight of sample. The xenon released was weighed separately to provide a mass balance. The purity of the xenon released was established to be better than 99% by mass spectroscopy. Two samples weighing 0.0911 and 0.1920 g. were analyzed in this way and atom ratios of F to Xe of 6.0 and 5.9 were obtained, in agreement with the formula XeF₆.

An attempt to confirm the formula, XeF₆, by mass spectroscopy was only partially successful. At first, the peaks of highest mass obtained were the XeF₄⁺ group. Seasoning of the mass spectrometer manifold with PtF₆ did not change the XeF₆ spectra, but allowed the PtF₆ mass spectrum to be obtained. Spectra initially showing the XeF₅⁺ group in greatest intensity (except for Xe⁺) were obtained by condensing the