The Heat of Formation of Krypton Difluoride[1]

Sir:

No thermochemical data for krypton compounds seem to have yet appeared in the literature. In the present work, the heat of thermal decomposition of krypton difluoride to its constituent elements has been measured.

The calorimetric method employed a system similar to dropping calorimeters used for enthalpy determinations. The "furnace," however, was at 25.0°, a temperature at which KrF_2 decomposes only slowly, and the receiving aneroid calorimeter[2] was at 93°, where KrF_2 decomposes rapidly to $Kr + F_2$. The KrF_2 samples were loaded into 78-ml cans of 0.013-cm thick stainless steel, through short Kovar-joined glass tubulations which were then sealed off. Five minutes before drop time, the cans were warmed from -196 to 25°. After the first (decomposition) drop measurement, the can was raised to the 25.0° zone, the calorimeter heated to its original starting temperature, and the drop measurement repeated. The difference between the two temperature changes of the calorimeter, multiplied by its heat capacity, gives the heat of decomposition of the sample at 25°.

Krypton difluoride was prepared by the method of MacKenzie and Fajer.[3] Vapor pressures were measured with a Monel Bourdon gauge: 10 ± 1 mm at $-15.5°$, 29 ± 2 mm at 0.0°, and 73 ± 3 mm at 15.0°. These are very close to the pressures given by Grosse, *et al.*,[4] attributed to KrF_4, but with a slope of log p *vs.* T^{-1} about 10% greater; ΔH_{subl} is 9.9 kcal mole^{-1}. Schreiner, Malm, and Hindman[5] gave a value of roughly 30 mm at 0°. The decomposition rate at room temperature as a gas in a Monel and stainless steel system was *ca.* 10% hr^{-1}, and as a solid, substantially lower.

Before loading the calorimeter cells, they were treated overnight with fluorine, at a temperature initially 130 to 150° which gradually decreased. This should minimize attack upon the cell by KrF_2 at 25° or by the F_2 liberated at 93° in the calorimeter.

The amount of reaction was determined after the calorimeter run in up to three ways: volume of total gas recovered from the cell (three runs); volume of krypton recovered (all runs); weight loss of cell upon removal of the gases (eight runs). The cell was weighed and attached to a vacuum system with wax, and the tip of the glass tube was broken off. In the last three runs, the first section of the system included a Monel Bourdon gauge and a calibrated volume to permit measurement of the total gas. The fluorine was then removed by passage through an activated copper catalyst (in earlier runs, by transferring the gas mixture with a Toepler pump to a bulb in which it was shaken overnight with mercury) and the krypton was transferred by a Toepler pump to a gas buret and measured, its purity subsequently being checked by mass spectrometry. The cell was back-filled with hydrogen or helium, removed from the vacuum line, stoppered, cleaned of wax, and reweighed. The three methods of analysis were all consistent with the assumption that the cell contained an equimolar mixture of Kr and F_2.

From the extrapolated vapor pressure of 138 mm at 25.0°, the 78-ml cell would contain 0.58 mmole of KrF_2 at saturation. Five runs were made with from 0.30 to 0.44 mmole of KrF_2; results were 14.2, 18.3, 13.8, 14.7, and 14.9 kcal mole^{-1} for $-\Delta E_1$.

$$KrF_2(g) \longrightarrow Kr(g) + F_2(g) \tag{1}$$

Four runs were made with from 1.31 to 1.54 mmoles of KrF_2. A correction of 9.3 cal mmole^{-1} was added for the KrF_2 in excess of 0.58 mmole to account for ΔE_{subl}; results for $-\Delta E_1$ were 13.6, 14.3, 14.6, and 13.9 kcal mole^{-1}. Rejecting the anomalous 18.3, the average is 14.2. Converting to constant pressure, $\Delta H_f°(KrF_2(g)) = +13.7$ kcal (mole^{-1} and $\Delta H_f°(KrF_2(c)) = +3.7$ kcal mole^{-1}. Using $+18.88$ for $\Delta H_f°(F(g))$ the thermochemical bond energy E(Kr–F) is 12.0 kcal, compared with 31 to 33 for E(Xe–F) in XeF_2, XeF_4, and XeF_6.[6]

Measurements are continuing and a more detailed report will be published at a later date.

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Oxidation of Molecular Nitrogen by Excited Singlet Oxygen Molecules in Aqueous Solution

Sir:

Excited singlet oxygen molecules in solution were shown to be formed in the reaction of H_2O_2 with HOCl (or Cl_2)[1–3] or with alkaline pyrogallol,[4] in the thermal decomposition of benzoyl peroxide,[5] as well as in certain photosensitized oxidation reactions.[6,7] The nature of these species has been discussed as well as their mode of decay.[7–9] Excited oxygen molecules were shown to be capable of oxidizing unsaturated organic compounds in solution.[6,7,10,11] An interaction between $^1\Sigma O_2$ and molecular nitrogen was demonstrated in the gas phase;[12]

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