Communications to the Editor

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 $-\Delta E_1$.

$$KrF_2(g) \longrightarrow Kr(g) + F_2(g) \qquad (1)$$

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, $\Delta H_f°(\text{Kr-F}_2(g)) = +13.7$ kcal (mole^{-1} and $\Delta H_f°(\text{KrF}_2(c)) = +3.7$ 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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Table I. Oxidation of N_2 to NO_3^- by Excited O_2 Molecules[a]

$[H_2O_2]$, *M*	Additive	[Additive], M^{-1}	pH	$[NO_2^- + NO_3^-]$[b]
0.8	NaOCl	0.025	13	$5 \pm 1 \times 10^{-5}$
0.8	NaOCl	0.05	13	$1.2 \pm 0.3 \times 10^{-4}$
0.8	NaOCl	0.1	13	$3.3 \pm 0.6 \times 10^{-4}$
0.4	NaOCl	0.1	13	$8 \pm 1 \times 10^{-5}$
0.2	NaOCl	0.1	13	$4 \pm 1 \times 10^{-5}$
0.8	$NaMnO_4$	0.2	0	$1 \pm 0.2 \times 10^{-4}$
0.8	$NaMnO_4 + Er(ClO_4)_3$	0.2 + 0.1	0	$1 \pm 0.2 \times 10^{-4}$
0.8	$NaMnO_4$	0.2	12	$1 \pm 0.2 \times 10^{-4}$
0.8	K_2CrO_4	0.2	0	$1.2 \pm 0.2 \times 10^{-4}$
0.8	K_2CrO_4	0.2	13	$1.4 \pm 0.3 \times 10^{-4}$
0.8	$Ti_2(SO_4)_3$	0.2	0	$<10^{-6}$
0.8	$Fe_2(SO_4)_3$[c]	0.1	0	$<10^{-6}$
0.8	$FeSO_4$[c]	0.05	1	$<10^{-6}$
0.8	$Ce(ClO_4)_4$	0.1	0	$<10^{-6}$
0.8	Catalase[d]	10^{-5}	7.5	$6 \pm 1 \times 10^{-5}$
0.25	Catalase	10^{-5}	7.5	3 ± 0.5
0.1	Catalase	10^{-5}	7.5	2 ± 0.3
0.01	Catalase	10^{-5}	7.5	1.6 ± 0.3

[a] Experiments carried out under 100–120 atm of N_2; $[N_2] = 10^{-1}$ *M*. [b] Concentration of $NO_2^- + NO_3^-$ in reaction mixture at the end of reaction, corrected for NO_3^- content of the reagents. NO_3^- content of the reagents $<3 \times 10^{-6}$ *M*. [c] Reaction mixture left overnight to complete catalytic decomposition. [d] Bovine liver catalase.

however, the chemical products of this reaction were not investigated. In the present study it has been shown that excited oxygen molecules produced by the oxidation of H_2O_2 in aqueous solution are capable of oxidizing nitrogen molecules to nitrate ions. It is suggested that this unique oxidation reaction could be used as a criterion for the mechanism of oxidation of hydrogen peroxide.

The oxidation of N_2 was carried out in a specially designed pressure vessel[13] which facilitates the mixing of two liquids while under gas pressure up to 200 atm. A concentrated evacuated solution of H_2O_2 (1 ml) was sealed in a half-filled glass vial. The vial was immersed in 10 ml of a solution of the other reagent which was saturated with N_2 under a pressure of 100–120 atm. The reaction was started by crushing the glass vial to pieces. After the reaction was over, the pressure was released and the residual H_2O_2 decomposed over Pt black. The nitrate present in a 2-ml aliquot was reduced by ammoniacal zinc powder in the presence of 0.1% Mn^{+2} to inhibit the reduction of NO_2^-.[14] The NO_2^- content was determined with Griess reagent according to Sawicki, *et al.*[15] Transition metal ions present in the reaction mixture, which interfere with the NO_3^- determination, were removed by precipitation with ammonia, followed by passing through a cation exchanger. In each case, a known amount of nitrate was added to another aliquot of the examined solution, and the total NO_3^- content was determined to assure the quantitativeness of the NO_3^- assay. Control experiments were carried out with argon instead of nitrogen to determine contaminants or artifacts in the analytical procedure. A blank experiment with $N_2 + H_2O_2$ in the absence of any oxidant showed that no oxidation of N_2 takes place, unless H_2O_2 is oxidized *in situ* in the presence of nitrogen. Under neutral and alkaline conditions NO_2^- was determined by the same procedure before reducing the NO_3^-; some NO_2^- was found amounting to 10–30% of the total $NO_2^- + NO_3^-$. The results were, however, much less reproducible than the $NO_2^- + NO_3^-$ values, owing to the fact that nitrite is oxidized to nitrate under the experimental conditions.

The results are summarized in Table I.

From the results it may be concluded that nitrogen is oxidized to NO_3^- when H_2O_2 is oxidized by hypochlorite, permanganate, and chromate, all of which are capable of double-equivalent oxidation. On the other hand, single-equivalent oxidation of H_2O_2 by Ce(IV) or by OH radicals (produced by Ti(III) + H_2O_2)[16] does not induce the oxidation of nitrogen. No oxidation of N_2 was detected following $H_2O_2 + Fe^{+2}$ (Fe^{+3}) reactions. This suggests that FeO^{+2}, if formed,[17] reacts with H_2O_2 by a single electron-transfer mechanism.

The oxidation of N_2 is most probably due to the action of singlet excited oxygen molecules. No oxidation of molecular nitrogen by OH or HO_2 radicals was observed, as is expected from their thermodynamic properties.[18] $^1\Delta_g$ O_2, which possesses $\Delta H = +22.5$ kcal/mole,[7,8] may eventually overcome the inertness of the N-N molecule. $^1\Sigma_g$ O_2 molecules are expected to react with water at an extremely fast rate;[19] thus it is rather unlikely that they are involved in the oxidation of N_2 under our experimental conditions. Singlet excited O_2 molecules may be produced from H_2O_2 only by double-electron-transfer oxidants. (The absence of oxidation of N_2 in the presence of Ti(III), Ce(IV), or Fe ions could eventually be interpreted as a result of deactivation of O_2^* by paramagnetic ions; this is, however, refuted by the erbium ion experiments.)

The oxidation of N_2 by $^1\Delta_g$ O_2 proceeds most probably *via* N_2O_2 as intermediate, which undergoes further oxidation either by H_2O_2 or O_2 to $N_2O_3 \rightarrow 2NO_2^-$ or $N_2O_4 \rightarrow NO_2^- + NO_3^-$, respectively. $N_2 + O_2^*$ do not form 2NO as this would require over 43 kcal/mole. As NO_2^-, which was found to undergo oxidation under the experimental conditions, is not oxidized either by H_2O_2 or by OCl^- in alkaline solution, $^1\Delta_g$ O_2 may also

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be involved in the advanced stages of nitrogen oxidation. Any more detailed mechanism would be highly speculative before some tracer experiments are carried out.

The yield of oxidized nitrogen ranges between 0.05 and 0.5% calculated on the basis of N_2. If it is calculated, however, on the basis of $^1\Delta_g\ O_2$ present in the $OCl^- + H_2O_2$ reaction, which is about 10% of the total O_2^*,[19] and taking into account that at least two $^1\Delta_g\ O_2$ molecules are required to oxidize N_2 to $2NO_3^-$, one obtains a yield >5% for the $N_2 + {}^1\Delta_g\ O_2$ reaction.

The oxidation of N_2 by H_2O_2 induced by catalase deserves a special emphasis. First it confirms the suggestion[20] that catalase or complex I oxidizes H_2O_2 by a double electron transfer, probably by a kind of hydride transfer.[17] Second, it demonstrates that the oxidative action of catalase may be due, at least in part, to the action of singlet excited O_2 molecules. This may be distinctive from the oxidative action of peroxidases.[20] A third point of biochemical interest is the possibility of oxidative nitrogen fixation which may, in spite of the extremely low yields obtained under our experimental conditions, contribute to the nitrogen cycle, in view of the widespread autoxidative processes in nature.

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Bis(cyclopentadienyl)zirconium

Sir:

Although there have been several reports relating to efforts to synthesize and characterize bis(cyclopentadienyl)titanium,[1] we are unaware of any attempts to produce the zirconium analog. We report here the synthesis and certain properties of bis(cyclopentadienyl)zirconium; the procedure employed was closely similar to that described previously.[1] The reaction involved is

$$(C_5H_5)_2ZrCl_2 + 2NaC_{10}H_8 \longrightarrow (C_5H_5)_2Zr + 2C_{10}H_8 + 2NaCl$$

In a typical experiment, 12.77 g (43.7 mmoles) of $(C_5H_5)_2ZrCl_2$, 2.01 g (87.4 g-atoms) of Na, *ca.* 12 g of $C_{10}H_8$ (10% molar excess), and 150 ml of tetrahydrofuran (THF) (freshly distilled over sodium benzophenone) were brought together in a 250-ml flask containing dry helium. The anhydrous, oxygen-free atmosphere was maintained while the reaction mixture was stirred for 24 hr. The THF was removed by distillation under reduced pressure and the residue was extracted with benzene which was freshly distilled after having been degassed with dry nitrogen and dried over $LiAlH_4$. Benzene was removed from the resulting dark purple (almost black) solution under reduced pressure. Naphthalene was removed from the solid residue by sublimation for 10 hr at 100° and 10^{-2} mm to provide 8.5 g (88% yield based on Na) of small purple-black, chlorine-free, *pyrophoric* crystals, mp >300° dec. Further removal of the last traces of $C_{10}H_8$ was accomplished by sublimation from small portions of the crude product over 10 hr at 150° and 10^{-3} mm. The importance of maintaining an anhydrous, oxygen-free atmosphere of high integrity throughout all of these operations cannot be overemphasized.

Anal. Calcd for $(C_5H_5)_2Zr$: Zr, 41.2; C, 54.2; H, 4.55. Found: Zr, 40.0; C, 54.2; H, 4.58.

Zirconium was determined by oxidation to ZrO_2 and the results were uniformly low; this is believed due to small but unavoidable losses of the sample in the initial stages of the extremely exothermal oxidation. In contrast to the titanium analog,[1] however, the analytical data for carbon and hydrogen were consistently satisfactory.

Thus far we have been unable to find a solvent in which $(C_5H_5)_2Zr$ is sufficiently soluble to permit a determination of molecular weight; this is a point of particular interest since the titanium analog was found to be dimeric.[1]

Using a modified Curie-Cheneveau balance calibrated with $HgCo(SCN)_4$, $(C_5H_5)_2Zr$ was found to be diamagnetic at 25°; this was confirmed by an esr spectrum of a sample of the solid.

X-Ray diffraction patterns were obtained using Cu Kα radiation (Ni filter), 35 kv, 15 ma, and exposure times of 16-20 hr; relative intensities were estimated visually. The *d* spacings (Ångstrom units) and relative intensities (in parentheses) found were: 7.3 (0.3), 5.8 (0.8), 5.2 (0.4), 4.5 (1.0), 4.1 (0.4), 3.5 (0.2), 3.4 (0.2), 3.0 (0.2), 2.5 (0.2), and 1.9 (0.3). Thus it is apparent that $(C_5H_5)_2Zr$ and $(C_5H_5)_2Ti$ are isomorphous.

The infrared spectrum of $(C_5H_5)_2Zr$ (Nujol mulls) included the following bands: 730 (m), 800 (s), 843 (w), 893 (w), 1015 (m), 1042 (w), 1063 (w), 1128 (w), 1165 (w), 1210 (w), and 1262 (w) cm^{-1}; there were no bands in the 2000-cm^{-1} region that could be attributed to Zr-H bonds. In general, the infrared spectrum of this compound was less well resolved than that of the corresponding titanium compound; otherwise the two spectra are closely similar, as expected. Efforts to obtain an nmr spectrum in benzene or toluene failed because of either limited solubility or interference by the solvent.

Bis(cyclopentadienyl)zirconium is appreciably soluble in benzene, toluene, *n*-hexane, and THF at 25°; the solubility in benzene at 5° is very low. When $(C_5H_5)_2Zr$ is heated to 300° at 10^{-3} mm, it turns black and sublimes very slowly; the vapor pressure is qualitatively much lower than that of the titanium analog. The infrared spectrum of the black solid residue was substantially the same as that of the starting material, thus providing no evidence of decomposition.

Air oxidation of $(C_5H_5)_2Zr$ yielded products that varied in both color (yellow to orange) and composition depending upon conditions and rate of reaction. These products were insoluble in a wide variety of solvents, the infrared spectral bands were quite broad, and the

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