# SYNTHESIS OF KRYPTON DIFLUORIDE USING A THERMALLY
GENERATED FLOW OF ATOMIC FLUORINE

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At present the synthesis of thermally unstable compounds, such as O_2F_2, NOF_3, and KrF_2, is done using low-temperature, nonequilibrium methods such as electrical discharge, ionization, and UV radiation to generate atomic fluorine [1]. This approach seems quite reasonable as these generate dissociated molecular fluorine in a reaction medium at low temperatures so that the end products can be stabilized. Thermally generated atomic fluorine is not used because molecular fluorine is not significantly dissociated until 500-600°C is reached, i.e., at temperatures where thermally unstable compounds could not exist.

However, the required nonequilibrium conditions in the reaction system using thermally generated atomic fluorine can be attained in spatially separated zones for the dissociated molecular fluorine and the low-temperature reaction with atomic fluorine. The transfer of atomic fluorine to the reaction zone could be provided by diffusion as the most simple case. Thus, at 950°K and 40 mm pressure, the equilibrium density of atomic fluorine is $1.23 \cdot 10^{17}$ cm^{-3} (the degree of dissociation is 0.323 [2]). The diffusion current of atomic fluorine at a distance of 1 cm from the generation zone at thermodynamic equilibrium and at a temperature gradient of 900 deg/cm is $3 \cdot 10^{18}$ cm$^{-2} \cdot$ sec^{-1}. Such a diffusion current is quite adequate for use in preparative synthesis. In order for this to be realized in practice, it is necessary that the rate of dissociation in the generation zone be equal to, or larger than, the rate of diffusion of the migrating atoms. The rate of homogeneous dissociation of molecular fluorine ($F_2 + F_2 \rightarrow F + F + F_2$) under the conditions given is $6 \cdot 10^{17}$ cm$^{-3} \cdot$ sec^{-1} (using the value log $K_{dis} = 12.66 - 14340/2.303T$ [2]). Evidently, to achieve these conditions it is necessary to catalyze the dissociation reaction of the fluorine. The usual activation energy of dissociating a molecule at a surface is approximately two or three times below the activation energy required for a homogeneous process ($E = 28.4$ kcal/mole [2]) due to the difference of enthalpy of adsorption of atoms and molecules on surfaces.

Writing the rate constant of the process

$$F_2 + Cat \rightarrow F + F + Cat$$
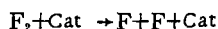
in the form k(cm$^{-2} \cdot$ sec^{-1}) $\simeq N \cdot e^{-11000/RT}$ (where N is the number of molecules of fluorine colliding with the catalyst surface), we can estimate the rate of heterogeneous dissociation as $2 \cdot 10^{19}$ cm$^{-2} \cdot$ sec^{-1}, where the above-mentioned catalyst is used under the conditions described. In order to demonstrate the possibility of using the above method of generating atomic fluorine to produce thermally unstable compounds, we carried out the synthesis of krypton difluoride ($\Delta H_0 = +14$ kcal/mole [4]), using thermally dissociated molecular fluorine. It is necessary to have a spatially separated zone between the generation of atomic fluorine and the synthesis of krypton difluoride. This is achieved by creating a high thermal gradient (300-1000 deg/cm) between these zones and by using a catalyst in the reaction to dissociate the molecular fluorine. Metallic nickel was used as the catalyst.

The formation of krypton difluoride was carried out in a reactor whose walls were cooled with liquid nitrogen (t = −196°C) (see Fig. 1), and coated with solid krypton. Atomic fluorine was generated by heating the surface of a nickel catalyst placed coaxially in the cylindrical reactor to 600-700°C.

The krypton difluoride formed was collected in an injection trap (t = −78°C) after cooling the catalyst and warming the reactor to room temperature. The amount of KrF_2 formed was determined by weight and its purity determined by IR spectral analysis from the band intensity at 595 cm^{-1} [4], after a preliminary calibration of the UR-20 spectrophotometer.

TABLE 1. Synthesis of KrF$_2$ Using Thermocatalytic Dissociation of Molecular Fluorine*

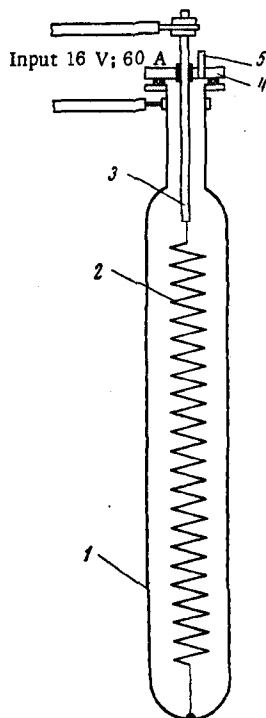| Distance between catalyst and Kr surface, cm	Temp., °C	Synthesis time, h	Yield of KrF$_2$, g
1	680	1	6
2	680	1	5
4	680	1	2,8
1	520	10	11,3

*Heater power $\simeq$ 1 kW.

Input 16 V; 60 A

Fig. 1. Basic reactor schematic: 1) reactor housing; 2) spiral heater; 3) insulated current lead-in; 4) flange; 5) connecting tube for exhaust and input.

The conditions and results of some typical experiments are presented in Table 1.

The fluorine pressure in the reacting systems was maintained at 30-40 mm in all of the experiments.

The results obtained showed that using thermal generation of atomic fluorine to synthesize thermally unstable compounds is not only possible, but also ensured yields of krypton difluoride equal to, and under some conditions (see Table 1), exceeding those described previously [4-6].

It is of interest to estimate the yield of krypton difluoride relative to the rate of diffusion of the atomic fluorine:

$$2qN_0/M\tau S\Phi,$$

where q is the yield of KrF$_2$ (g); N is Avogadro's number; M is the molecular weight of KrF$_2$ (g); τ is the time for synthesis (sec); S is the area of the catalyst surface (cm^2); Φ is the coefficient of effective use of atomic fluorine. The value of Φ is estimated from the quantum yield of KrF$_2$ in the system solid krypton—gaseous fluorine [6] to be 0.02. With this value the diffusion current is $1.96 \cdot 10^{18}$ cm$^{-2} \cdot$ sec^{-1}, which is in good agreement with the estimate $3 \cdot 10^{18}$ cm$^{-2} \cdot$ sec^{-1}.

The catalytic effect of the hot nickel surface is demonstrated by the dependence of the rate of synthesis of krypton difluoride on the method of pretreatment of this surface. Thus, a preliminary annealing of the catalyst

in an oxygen atmosphere at least doubles the rate of formation of krypton difluoride. However, if the oxygenated and fluorine-treated catalyst is then annealed in a vacuum or in a fluorine atmosphere at 800°C, the rate of the process falls by about a factor of 10.

We assume that the catalyst accelerates the stage of dissociation of molecular fluorine, as no other process is possible at the hot surface of the catalyst with this system, according to thermodynamic considerations. These deductions are indirectly confirmed in principle by the increased yield of KrF_2 with decreased distance between the catalyst surface and the solid krypton, because this increases the diffusion flux of atomic fluorine at the krypton surface. This same acceleration of the process of dissociation of molecular fluorine by some metals probably explains their catalytic effect on the process of fluoridating Xe [7, 8]. We consider improbable the hypothesis of the authors that the catalytic mechanism is based on the formation of complex compounds on the surface of the catalyst, including xenon fluoride. It is interesting that Baker [7] quotes a constant for the rate of formation of xenon difluoride ($k = 10^{21}e^{-(10400 \pm 1500)/RT}$) which is in good agreement with our estimate of the constant for the catalytic dissociation of molecular fluorine ($K = 7 \cdot 10^{21}e^{-11000/RT}$).

Finally, the thermocatalytic dissociation of molecular fluorine has been applied to the synthesis of other thermally unstable compounds, such as dioxydifluoride, fluorides, and oxyfluorides of chlorine and of nitrogen. The results of this work will be published.

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NEW METHOD FOR THE SYNTHESIS OF ORGANOMETALLIC
DERIVATIVES OF TRANSITION METALS IN LOWER OXIDATION STATES

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The reactions of $TiCl_4$ with organometallic compounds of elements of groups I-III, in which the organic radical does not contain hydrogen in the β position to the metal, are known to form the reasonably stable compounds R_4Ti [1, 2]. In many cases it is possible to prepare in quantitative yield the corresponding organohalo derivatives of titanium(IV), R_nTiCl_{4-n} (n = 1-3) with Ti–C σ bonds, where R is trimethylsilylmethyl, benzyl, etc. [3, 4].

Reactions of compounds of group I-III metals with $TiCl_3$ do not form the corresponding R_3Ti. Thus tribenzyltitanium cannot be prepared by reaction of $TiCl_3$ with $C_6H_5CH_2MgCl$. The primary products of the reaction of $TiCl_3$ with $LiCH_2SiMe_3$ ($RTiCl_2$ and R_2TiCl) disproportionate in quantitative conversion to R_2Ti^{II} and R_4Ti^{IV} [5, 6].