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INFRARED FLUORESCENCE OF HYDROGEN FLUORIDE DURING MULTIQUANTUM DISSOCIATION OF A MIXTURE OF CF₃OF WITH H_2

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The study of the dissociation of complex molecules during excitation by a pulsed CO_2 laser is one of the urgent problems of laser chemistry. In the present work, the dissociation of complex molecules during excitation by a pulsed CO_2 laser is one of the urgent problems of laser chemistry. In the present work, the dissociation of molecules of trifluoromethyl hypofluorite CF_3OF in a mixture with hydrogen H_2 in the pulsed CO_2 laser emission field is discussed. This compound attracted attention because carbon-13 and oxygen-18 isotopes could possibly be obtained by laser excitation.

Trifluoromethyl hypofluorite CF_3OF is a colorless gas with a high fluorescing capacity. The energy of the C-F bond is 487.3, C-O 356.1, and O-F 196.9 kJ/mole [1]. In the frequency region of 4000-400 cm⁻¹, in a gaseous state, eight IR absorption bands are observed. One of them, with a maximum of the absorption band at 947.3 cm^{-1} , falls within the generation region of the CO₂ laser. The gaseous phase was irradiated by a pulsed CO₂ laser. The energy in the pulse reached 12 J at a pulse duration of 150 nsec at halfheight. The working reactor consisted of a stainless steel cuvette with NaCl windows, sealed at the ends of the cuvette by Teflon and indium washers. The composition of the initial mixture and also of the products of the laser-chemical reaction were controlled by IR spectra on a IKS-29 spectrophotometer and mass spectra on a MI-1201 mass spectrometer. Difluorophosgene COF₂ and hydrogen fluoride HF were found to be the products of the laser-chemical reaction. The reaction of CF₃OF with H₂ was studied over a wide range of hydrogen pressures at different partial pressures of the reagents and intrinsic pressures of CF3OF. The frequency of the laser emission was selected as 931 cm⁻¹, taking into account the "red" shift of 16 cm⁻¹ arising during multiphoton dissociation of the molecules. The energy density of the laser emission was not less than 8.5 J/cm^2 . Figure 1 shows the dependence of the dissociation yield β on the hydrogen pressure and intrinsic pressure of trifluoromethyl hypofluorite. The maximal value of the dissociation yield is 10%, and this value decreases inappreciably when the hydrogen pressure is increased. The dependence of β on the intrinsic pressure is different. Figure 1b shows a sharp increase in β at CF₃OF pressures higher than 80 Pa. The mixture in the reactor is completely depleted during one single laser pulse. The quantitative measurements at the 1929 cm⁻¹ band with respect to the same band for pure COF_2 showed a complete conversion of CF_3OF into COF_2 . From the data of the analysis of the dissociation products and the character of the dependence of the dissociation yield on the pressure we can conclude that under given conditions a chain laser-chemical reaction takes place

$$CF_3OF + H_2 + nhv \rightarrow COF_2 + 2HF$$

k

and we can assume that the dissociation of CF_3OF proceeds by chain mechanism

$$CF_3OF + nhv \rightarrow CF_3O^* + F^*,$$
 (1)

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 45, No. 5, pp. 785-790, November, 1986. Original article submitted June 21, 1985.



Fig. 1. Dependence of dissociation yield β of CF₃OF molecules on hydrogen H₂ (a) and CF₃OF pressure (ratio of partial pressures of CF₃OF and H₂ 1:3) (b); P_{CF₃OF} = 266 Pa, E_{1as} = 8.5 J/cm².

$$F' + H_2 \rightarrow HF^* + H', \quad \Delta H \approx -134 \text{ kJ/mole}$$
 (2)

$$H + CF_3 OF \rightarrow CF_3 O^* + HF^*, \Delta H \approx -356 \text{ kJ/mole}$$
 (3)

$$CF_3O^* \rightarrow COF_2 + F$$
, $\Delta H \approx +92$ kJ/mole (4)

$$CF_3O^* + H_2 \rightarrow COF_2 + HF^* + H^*, \quad \Delta H \approx -126 \text{ kJ/mole}$$
 (5)

$$\underset{H^{+}+M \rightarrow 1/2H_{2}+M,}{\overset{k_{ST}}{}}$$
(6)

$$HF^{*} \rightarrow hv_1 + HF,$$
(8)

$$HF^* + H_2 \rightarrow H_2^* + HF,$$
(9)

$$HF^* + H_2 \rightarrow H_2 + HF,$$
(10)

$$H_{2}^{\star}+M \rightarrow H_{2}+M, \qquad (11)$$

$$HF^* + M \rightarrow HF + M.$$
 (12)

Radicals H[•], F[•], CF_30^* are active centers. Reactions (2), (3), (4), (5) are chain propagation reactions. A chain termination takes place in reactions (6), (7). Reaction (8) is, in particular, worth mentioning. If the proposed dissociation mechanism of the CF_30F molecule does in fact correspond to the process taking place, then a study of the emission spectra of hydrogen fluoride may serve to confirm the paths of occurrence of the chain reaction.

To record this emission, a cuvette made of stainless steel with two perpendicular cylindrical channels was used. The time-dependent resolution of the recording system is not less than 1 μ sec. The spectral region was isolated by a set of light filters IKR-1, IKS-3, IKS-5, IKS-7, and NS-1, NS-2, NS-3. To increase the accuracy of the experiment, the pressure in the



Fig. 2. Oscillogram of fluorescence pulse of hydrogen fluoride, obtained by using a S8-14 oscillograph (sensitivity 0.2 V/scaling, scanning 100 usec/scaling).

Fig. 3. Calculation-theoretical dependence of [HF*] on time for b/m = 10 (a), 50 (b), 100 (c).

cuvette was fixed at 1.06 kPa at a 1:3 ratio between the reagents. A typical oscillogram of the fluorescence pulse is shown in Fig. 2. The observed pattern contains an exciting laser pulse, and directly the fluorescence pulse itself. At the rear-front of the fluorescence, three maxima are observed. Their position does not change according to the experimental conditions. Their presence can be explained by a reflection of a pressure gradient wave (with a sonic frequency) from the windows and walls of the working cuvette. In the cuvette construction used, the sonic rate in the gas mixture studied is ~780 m/sec. Therefore, at given cuvette dimensions, luminescence maxima were produced with an off-time ratio of 100 µsec.

The lag between the exciting pulse of the laser and the fluorescence pulse is due to the induction time. A detailed description of the induction time depends on the method of observations and its sensitivity. In our case, the fluorescence signal is most probably observed completely from the whole photometric cell, and therefore the value of the induction time is so considerable.

If the schemes of reactions (1)-(12) are correct, they should describe the form of the fluorescence pulse. We assumed that the fluorescence intensity is proportional to HF* concentration and deduced this dependence. From the scheme of reactions, we can write

$$\frac{d[CF_{3}OF]}{dt} = -k_{0}[CF_{3}OF] - k_{2}[CF_{3}OF][H^{-}], \qquad (13)$$

$$\frac{d[CF_{3}O^{*}]}{dt} = -k_{3}[CF_{3}O^{*}] + k_{0}[CF_{3}OF] + k_{2}[H^{*}][CF_{3}OF] - k_{4}[CF_{3}O^{*}][H_{2}], \qquad (14)$$

$$\frac{d[H^{\cdot}]}{dt} = k_1[F^{\cdot}][H_2] - k_2[H^{\cdot}][CF_3OF] + k_4[CF_3O^{\star}][H_2] - k_{st} [H^{\cdot}][M],$$
(15)

$$\frac{d[\text{HF}^*]}{di} = k_1[F^*] - k_2[\text{H}^*][\text{CF}_3\text{OF}] + k_4[\text{CF}_3\text{O}^*][\text{H}_2] - k_6[\text{HF}^*] - (k_8 - k_7)[\text{HF}^*][\text{H}_2] - k_{10}[\text{HF}^*][\text{M}].$$
 (16)

The solution of Eqs. (13)-(16) is a fairly complex problem. However, the system becomes simplified if a quasistationary concentration of the radicals is assumed. The solution of Eq. (13) will have the form

$$[CF_{3}OF] = [CF_{3}OF]_{0} \exp \left[-(k_{0} + k_{2}[H^{\cdot}])t\right].$$
(17)

As the deactivation proceeds more slowly than the remaining processes, the expression $k_{st}[H^{\circ}]$ [M] may not be taken into account (for reaction (6), the constant is ~10⁻³² cm⁶·sec⁻¹ [2]). Since the time of induction is high compared with the duration of exciting laser pulse, the consumption of CF₃OF by reaction (1) will play no role, and then the expression will acquire the following form

$$\frac{d[\text{HF}^*]}{dt} = 2k_2[\text{H}^*][\text{CF}_3\text{OF}] - (k_6 + k_{10}[\text{M}])[\text{HF}^*] - (k_7 + k_8) \frac{k_2[\text{CF}_3\text{OF}]}{k_4[\text{CF}_3\text{O}^*] + k_1[\text{F}^*]} [\text{HF}^*].$$
(18)

We shall introduce the following designations: $[HF^*] = x$; $2k_2[H^{\cdot}][CF_3OF]_0 = A$; $\frac{(k_7+k_8)k_2[H^{\cdot}][CF_3OF]_0}{k_4[CF_3O^*]+k_1[F^{\cdot}]} = B$; $k_6+k_{10}[M] = b$; $k_2[H^{\cdot}] = m$. Then (18) is written as

$$\frac{dx}{dt} = Ae^{-mt} - bx - Bxe^{-mt}.$$
(19)

At whole values of b/m, the particular solution acquires the form [3]

$$x = e^{-bt + \frac{B}{m}} e^{-mt} \left[Ae^{-\frac{B}{m}} e^{-mt} \sum_{k=1}^{n-1} \frac{(-B)^{k-1}}{m^k (n-1) (n-2) \dots (n-k) e^{-mt(n-k)}} - \frac{A (-B)^{n-1}}{m^n (n-1)!} E_i \left(-\frac{B}{m} e^{-mt} \right) + C_0 \right],$$
(20)

where E_i(x) is integral exponential function;

$$C_0 = -Ae^{-\frac{B}{m}} \sum_{k=1}^{n-1} \frac{(-B)^{k-1}}{m^k (n-1) (n-2) \dots (n-k)} + \frac{A(-B)^{n-1}}{m^n (n-1)!} E_i\left(-\frac{B}{m}\right); \quad n = \left[\frac{b}{m}\right].$$

We shall use the known rate constants for reactions (2), (8), (9), (10) [4]: $k_6 \ge 200 \text{ sec}^{-1}$; $k_7 \ge 1.4 \cdot 10^{-12} \text{ cm}^3/\text{sec}$; $k_8 \ge 0.63 \cdot 10^{-12} \text{ cm}^3/\text{sec}$; $k_{10} \ge 5 \cdot 10^{-13} \text{ cm}^3/\text{sec}$; $k_1 \ge 20 \cdot 10^{-12} \text{ cm}^3/\text{sec}$. The concentration of the radicals [H^{*}] can be calculated by assuming that it will be determined by the dissociation yield of CH₃OF. Under the experimental conditions, in the case when chain mechanism introduced inappreciable contribution, the highest dissociation yield is 10%. The concentration of the active centers is thus 7.6 \cdot 10^{14} \text{ cm}^{-3} at a CF₃OF pressure of 266 Pa. By solving equation (18) at known reaction rate constants and initial concentration of the hydrogen atoms, the [HF*] = f(t) dependences (Fig. 3) can be plotted. Figure 2 shows that the duration of the forefront of the fluorescence pulse is 50 µsec at a CF₃OF pressure of 266 Pa and H₂ pressure of 798 Pa. A comparison of the experimental (Fig. 2) and theoretical curves (Fig. 3) shows a good agreement at (b/m) = 30-60.

A limiting case of a high hydrogen pressure makes it possible to consider its concentration to be unchangeable during the chain reaction process. The solution of Eq. (18) will have a simple form

$$[HF^*] = A(e^{-m't} - e^{-b't}),$$
(21)

where $m' = k_2 \cdot [H']$; $b' = k_6 + (k_7 + k_8) \cdot [H_2] + k_{10} \cdot [M]$. A similar expression for [HF*] is given in [4]. As the experimental and theoretical curves correspond at $(b/m) \approx 30-60$, the rate of the reaction of CF₃OF with atomic hydrogen can be calculated

$$k_2 \cdot [\text{H}^{-}] \approx (4,67 - 2,3) \, 10^3 \, \text{sec}^{-}$$

and hence $k_2 \approx (3-6)10^{-12} \text{ cm}^3 \cdot \text{sec}^{-1}$.

It should be noted that the experimentally obtained duration of the rear front of the fluorescence pulse is lower than follows from the mathematical expressions. This is probably because in the deduction of Eq. (18), reactions (6) and (7), and also the reactions of radicals in between themselves were not taken into account. As a result of heating the mixture an overexcitation of the hydrogen fluoride molecules to energies sufficient for the dissociation of trifluoromethyl hypofluorite becomes possible, thus leading to a reaction

$$HF^{**}+CF_{3}OF \rightarrow COF_{2}+HF^{*}+F_{2}.$$
(22)

At present there are no direct proofs of the existence of such a reaction. The possible path of dissociation of CF_3OF may be also thermal decomposition.

It was thus shown that the dissociation of a mixture of trifluoromethyl hypofluorite with hydrogen (overall pressure up to 1.3 kPa) can be described by a scheme of reactions (1)-(12).

The rate constant of the reaction of trifluoromethyl hypofluorite with atomic hydrogen is ~10⁻¹² cm³/sec.

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TRANSFER OF ELECTRONIC EXCITATION ENERGY IN COVALENTLY-LINKED **PORPHYRIN DIMERS (ETHANE-**BISPORPHYRINS)

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UDC 535.37:535.737.2

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The existing methods of organic synthesis can be used for synthesizing dimers of complex organic molecules. In these dimers, such parameters as the distance between interacting dipoles and their mutual orientation determined by the dimer structure, can be varied. Covalently linked bisporphyrins of different structures [1-3] and chemical chlorophyll dimers [4, 5] are convenient systems for studying an excitation energy transfer and electron transfer as well as for mimicking basic photoprocesses which undergo in natural chlorophyll complexes in vivo.

Some earlier results [6, 7] show that for ethane-bisporphyrins, in which the monomers are linked in meso-positions by a -CH2-CH2- group, the intermolecular interactions determine spectral properties of the dimers (splitting of the Soret band) but have no effect on deactivation of singlet and triplet excited states. In mixed porphyrin dimers, composed of two different covalently linked molecules, there are substantial changes in spectral luminescence properties and energetic parameters of the complexes, which can be due to various reasons (excitation energy transfer, perturbation by central metal ion in porphyrins, etc.). The discovered effects are thoroughly analyzed in the present work with the special emphasis on spectral and structural parameters of the dimers. The mechanism for energy transfer in such systems is elucidated.

EXPERIMENTAL

Results were obtained for two different groups of chemical dimers. The first group consists of dimers containing two identical molecules (meso, meso'-ethane-bisoctapropylporphyrin (OPP)₂ and meso, meso'-ethane-bisoctapropylporphyinato-Zn(II) (ZnOPP)₂). The second group represents complexes, in which monomers either contain different metal ions in the center of the porphyrin cycle $((Zn + Cu)(OPP)_2)$ or one of the monomers is a free-base porphyrin (Cu-(OPP)2). The syntheses, structures, identification methods, and instrumentation are described elsewhere [6, 8]. It should be noted that for all studied dimers, the monomers were linked in meso-positions by a -CH2-CH2-* group. Results of 'H NMR studies [6] and independent x ray data [9] indicate that the planes of monomer macrocycles in ethane-bisporphyrins are practically parallel and do not overlap. Figure 1 presents a structure of the studied dimers corresponding to C₂h symmetry (local symmetry of meso-substituted monomers is C_{2V}). Most of our spectral luminescence measurements were done in EPA (diethyl ether-petroleum ether-isopropanol 5:5:2) in the temperature range 293-77°K. In order to eliminate any concentration effects as well as interactions between different dimers, the concentration was kept $<10^{-5}$ mole/liter.

*In some cases monomers can be linked by the ethylene group --CH=-CH-, so, in order to avoid ambiguity, our objects are called ethane-bisporphyrins.

Translated from Zhurnal Prikladnoi Spektroskopii, Vol. 45, No. 5, pp. 790-796, November, 1986. Original article submitted July 8, 1985.