VERY FAST CHEMILUMINESCENCE REACTION

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*Institute of Physics, Leningrad State University, Leningrad 198904, USSR***Abstracts.** Recombination of the $I(^2P_{1/2})$ and $I(^2P_{3/2})$ atoms accompanied by radiation

has been studied. Spectra and rate constants have been measured: $k_1 = 10^{10}$, 7^{+7}_{-4} , $3^{+3}_{-1.5}$ ($M = \text{He, Ar, CF}_3\text{CFICF}_3$, respectively); units, 10^{-15} photon cc/particle²s. It has been found out that the reaction (1) can be described by the complex formation mechanism. Process (1) can be considered as a representative of a wide class of recombination reactions accompanied by radiation which proceed by complex formation with particle M and have very high rate constants. The existence of such fast chemiluminescence reaction can make real creation of recombination lasers which operate at molecular transitions.

1. Introduction.

Electronic transition diatomic lasers have been a very active field of research in recent years. There is a constantly growing interest in development of chemical pumped visible and UV wavelength systems, recombination lasers, in particular. The halogens and interhalogens are a class of molecules that appears to be particularly attractive as working media of chemical lasers. In these cases the $\text{Hal}_2(B-X)$ transitions appear to have radiation and kinetic properties that make it attractive (see (1-3) and references therein). Unfortunately, kinetic information needed for creation of recombination lasers operating on $\text{Hal}_2(B-X)$ transition is very poor and contradictory (4,5). In recent years we have worked out the quantitative laser-induced chemiluminescence kinetic spectroscopy (QLICKS) method that enable us to obtain quantitative information about chemiluminescence rate constants and their spectral distributions (6). In this paper we present our study results concerning the iodine atom recombination accompanied by radiation

(here and later $I^* = I(5p^5\ ^2P_{1/2})$, $I = I(5p^5\ ^2P_{3/2})$, $I_2(B, v') = I_2(BO_u^+, v')$, $I_2(X, v'') = I_2(XO_g^+, v'')$) that has shown this reaction to be very attractive for creation of recombination laser.

2. Experimental setup and method of measurements.

Fig.1. Schematic diagram of the experimental apparatus.

The apparatus used is shown schematically in Fig.1. The I and I^* atoms were obtained in the photolysis of alkyl- and perfluoroalkyl iodides (RI) by $\lambda = 266$ nm radiation in photochemical chamber (PC) having four quartz windows. The chemiluminescence intensity was measured by means of calibrated system PMT + filter ($\lambda = 540 - 630$ nm). Pulsed AIG-Nd laser with double frequency doubling was used as a source of photolysing radiation. To form homogeneous intensity distribution of photolysing radiation over cross-section the laser beam scatterer (SR) was used in course of measurements of the chemiluminescence rate constants.

The measurements of individual pulse intensity (in arbitrary units) and average power (in absolute units) of laser radiation were made by the laser pulse energy meter (EM) and average power meter (PM) respectively. Chemiluminescence spectra $J_{Chl}(\lambda)$ were registered by the calibrated system monochromator + PMT. To increase chemiluminescence intensity in the courses of spectra measurements that, for example, for reaction (1) is proportional to I^* and I concentrations product $[I^*][I]$, laser radiation had been focused. PMT signals were measured by photon counter with time resolution of $\Delta t = 0,5 - 128 \mu s$ in the range of $t = 0.03 - 30$ ms. Signals accumulations was carried over series of 500 - 3000 laser pulses.

Reagents formed in the photodecomposition are spent in reactions, among whose of the most importance are (7):

The reagent concentration determination can be made only immediately after laser pulse, i.e. at $t \rightarrow 0$. Therefore k_1 calculations was proceeded by determination of the initial PMT signals from the kinetic dependences of $J_{Chl}(t)$ at $t \rightarrow 0$.

3. Results and discussion.

The products of alkyl- and perfluoroalkylidides photodecomposition can participate in six recombination reactions accompanied by radiation (1,7-11) (See (6) 8-12) and Fig.2):

$[I(t)] \cdot [R(t)]$ corresponds to the reaction (1).

Volume of this paper does not permit to describe the calculation procedure of the k_1 absolute values and their dependences on experimental conditions. One can find the details in (6). Here we will show only final results (Fig.4). One can see that k_1 values depend on M nature and [M] values. The errors in $[I^*] \cdot [I]$ calculation depends mainly on errors in [I] determination, since the latter is proportional to the I atom absolute quantum yields in RI photolysis determined with the accuracy not better than $\times 2$: $\Phi_I(\lambda) \approx 0,1$ (see (6:12) and references therein). The accuracy of k_1 determination is also equal to $\times 2$. On Fig.4 relative values of k_1 errors are represented.

Fig.4. Dependences of the reaction (1) rate constants on RI and M pressure. a: $[He] = 0$, $RI = CF_3I$ (1), CF_3CFICF_3 (2); b: $RI = CF_3I$ (1), CF_3CFICF_3 (2-4), $[RI] = 0.5$ Torr (1-2), 0.8 Torr (3-4), $M = He$ (1-2), Ar (3), and CO_2 (4). The bars in the plot show the errors of k_1 relative values.

We are aware of three works (8:9:14) dealing with the study of reactions (1,7). All of them have been performed at the same laboratory. The mechanism of reactions (1,7) has not been discussed in these papers. The rate constants for $I_2(B,v)$ formation has been estimated in (8) under the assumption, that reaction (1) is described by elementary processes:

One should add to the processes (12-14) the reaction

which has not been taken into account in (8). Analysis performed in (6) has shown that one can obtain the $k_1 = 1 \cdot 10^{-17}$ photon cc/particle²s taking into account the values of $k_{12} = (1 \pm 0,5) \cdot 10^{-32}$ cc²/s (8), $k_{13} = 1.6 \cdot 10^5$ s⁻¹, $k_{14} = 1.5 \cdot 10^{-10}$ cc/s for $I_2(B,v = 70)$, $k_{13} + k_{15} < 3 \cdot 10^6$ s⁻¹ for $I_2(B,v = 5 - 70)$, $T = 300$ K (15:16). This value is less approximately by a factor of 10^2 than that one obtained by us. We believe that the reason is experiment errors made in (8) in k_{12} determination (6).

We were surprised by the enormous k_1 values we have obtained. Combination of such values with the fact of its independence on $[RI]$ and $[M]$ for $[M] \gg [RI]$ and also with k_1 increasing at Ar and He addition makes the problem of our data interpretation rather difficult. The performed in (6) consideration of possible mechanism of reaction (1) has shown that neither reversed dissociation

nor kinetics of the energy transfer theory (reactions 13-18)

(here $I_2(B,v')$ is the state of $I_2(B,v'_{\max} - \Delta v)$ from that $I_2(B,v')$ dissociation to $I^* + I$ is impossible due to energetic reasons) do not enable to explain spectra obtained and k_1 values. In both mechanism framework k_1 values do not exceed 10^{-18} photon cc/particle² s and calculated chemiluminescence spectra disagree with experimental ones. The only mechanism that can explain data obtained is the complex formation one: the I^* (or I) atom forms complex I^*M (IM) which reacts with I (I^*) and this results in the $I_2(B,v)$ formation. Our data do not enable us to choose unambiguously between the two ways of complex formation. Let us consider one of them where complex I^*M is formed. This mechanism could be roughly describe as:

(here $(I^* \cdots M)$ is the collision complex whose excitation energy is equal to its dissociation one, I^*M is the stabilized complex). The data on mechanism and kinetics of I^* collision induced luminescence as well as of I^* deactivation in collision with M (see (17) and references therein) enable us to estimate the rate constants for elementary processes which describe reaction (1).

Here we shall not give the detailed analysis and will present only the final results of this description. The k_1 value is equal

$$k_{RI} = K_I^* R_I \frac{k_{RI}^{20}}{k_{RI}^{23}} k_{13} \quad (24)$$

(here $K_I^* R_I = k_{RI}^{19}/k_{RI}^{19}$), when $k_{RI}^{23} [RI] \gg k_{13} + k_{15}$ and $M = RI$. One can suppose that k_{RI}^{23} value does not depend on B, v (as are in the case $M = I_2, CO_2$) and is close to gas-kinetic rate constant. Apparently, the same can be said about k_{RI}^{20} . Let us assume that $k_{RI}^{20} = k_{RI}^{23}$ and take into account that $K_I^* R_I = 1.2 \cdot 10^{-20}$ cc (17). To calculate k_1 it is necessary to choose k_{13} and consequently B, v values populated in the interaction of $(I^* \dots M)$ and $I^* M$ with I . The B, v values can be roughly estimated by the position of the maximum of reaction (1) spectrum $\lambda \approx 580$ nm: it follows that maximum population is observed at $B, v = 14 - 16$ (6,18). The $k_{13} = 5 \cdot 10^5$ s⁻¹ corresponds for these levels (16). Having substituted the values of constants presented above into formula (24) we obtained $k_{RI}^{20} = 6 \cdot 10^{-15}$ photon cc/particle² s, which is very close to the experimental value. We have measured the $K_I^* He$ value to calculate the k_{He}^{20} one: $K_I^* He = 8 \cdot 10^{-22}$ cc (6). Assuming $k_{He}^{20} = 2 \cdot 10^{-10}$ cc/s and using $k_{He}^{23} = 7.5 \cdot 10^{-12}$ cc/s $\ll k_{RI}^{23}$ (19), we have obtained $k_{He}^{20} = 1.1 \cdot 10^{-14}$ photon cc/particle² s, which is quite close to the experimental value too. The k_{He}^{20} value larger than k_{RI}^{20} is provided by the smaller value k_{He}^{23} than that of k_{RI}^{23} . Thus, the model discussed describes adequately the obtained experimental data.

The system of JChI recording used here do not permit us to perform detailed study of reaction (7) kinetics. We have obtained the estimation of k_7 only: $k_7 = (3.5 \pm 1.7) \cdot 10^{-17}$ photon cc/particle² s at $[RI] = 4$ Torr, $RI = CF_3I, CF_3CFICF_3$.

We believe the process (1) to be a representative of a wide set of recombination reaction accompanied by radiation that proceed by complex formation with particle M being a third body, and have very high rate constants. Mechanism of these reaction can be described as reaction (1) one. The real "possible candidate" for similar reaction is the

where $Hal = Br(^2P_{3/2}), Cl(^2P_{3/2}), F(^2P_{3/2}), M = He$. Analysis has shown that rate constants $k_{25}(Hal = F, M = He) \approx 2 \cdot 10^{-12}$ photon cc/particle² s, for example.

Indirect evidence confirming the obtained results is presented in (2). The authors came to conclusion that reaction

exist and $k_{26} = 8 \cdot 10^{-11}$ cc/s. They are wrong in supposing that the reaction (26) which is the reversed dissociation (see above), has such a high value of rate constant. However the conclusion on the existence of fast chemiluminescence process in $I^* + F + He$ mixture seems to be correct. We think that the mechanism of this process is described by the reactions similar to the (13,15,19-23) ones.

The existence of such fast recombination processes accompanied by radiation can, in our opinion, make real creation of recombination lasers with chemical, photochemical or electrical discharge pumping, which operate on molecular transition.

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