Journal of Photochemistry, 5 (1976) 49 - 59

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KINETICS OF LUMINESCENCE OF BO AND BCl RADICALS FORMED DURING I.R. PHOTOLYSIS OF BCl_3 BY CO_2 LASER PULSES

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(Received August 27, 1975)

Summary

The results of kinetic studies of BO* and BCl* radical formation in strong ($\sim 10^9$ W/cm^2) CO_2 laser field are reported. The radicals are found to be built up in excited electronic states which caused a luminescence pulse. The rate constant was measured for boron oxide formation from the reaction of BCl_3 fragments with oxygen. Its value was estimated to be $K = (8 \pm 4) \times 10^5$ s^{-1} Torr^{-1}.

Introduction

The advent of high-power pulsed CO_2 lasers has opened the way for a new method of radical production, *i.e.* infra-red laser photolysis of molecules. As early as 1971 - 72 [1, 2], it was shown that a CO_2 laser pulse with an intensity ranging from 10^7 to 10^9 W/cm^2) may dissociate SiF_4, NH_3, C_3F_3Cl and some other molecules, the frequency of one of their vibrations being close to that of CO_2 laser radiation; the radicals SiF*, NH*, NH_2*, C_2* may be formed in excited electronic states. In the ensuing experiments on BCl_3 molecules [3], where the frequency of the ν_3 vibration coincides with that of the transition $00^01 \rightarrow 10^00$ of the CO_2 laser, we have demonstrated two dissociation stages: an instantaneous one arising with no delay following the CO_2 laser pulse (up to 0.03 Torr), and a retarded one arising when highly excited BCl_3 molecules collide. The instantaneous and retarded dissociation stages of SiF_4 molecules under a CO_2 laser pulse have also been observed by Isenor *et al.* [4]. Dissociation of BCl_3 molecules is followed by visible luminescence in the range 4400 - 6000 Å. Because of the instantaneous collisionless dissociation of BCl_3 molecules, it has been possible to separate successfully the ^{10}B and ^{11}B isotopes during selective dissociation of the $^{10}BCl_3$ or $^{11}BCl_3$ molecules by tuning the CO_2 laser radiation frequency to the pertinent absorption bands (995 and 956 cm^{-1}). Oxygen was used [5, 6] to bind the products

of BCl_3 dissociation. The chemical reaction between fragments of BCl_3 and O_2 molecules resulted in BO* radicals in the excited state $^2\Pi_{1/2}$, $^2\Pi_{3/2}$ and selectivity of $^{10}BCl_3$- and $^{11}BCl_3$-molecular dissociation and the subsequent chemical reaction of boron oxide formation were illustrated [5, 6] by the isotopic shift in the luminescence spectrum of $^{10}BO^*$ and $^{11}BO^*$.

The dissociation of BCl_3 molecules by a CO_2 laser pulse is followed also by luminescence in the region of 2720 Å. The spectrum of this luminescence coincides with that of the transition $A^1\Pi \rightarrow X^1\Sigma^+$ for the radical BCl* [6].

The object of the present paper is to study the kinetics of reaction for excited BO* radical formation and the kinetics of BCl* radical luminescence during I.R. photolysis of BCl_3 molecules in an intensive field of a CO_2 laser pulse, since these processes are very important for boron isotope separation [7].

Experimental

The kinetics of formation of excited radicals BO* and BCl* has been studied by investigating the luminescence pulse shapes. The experimental set-up is schematically illustrated in Fig. 1. A pulsed CO_2 laser produced pulses of up to 0.85 with a half-height length of 80 ns. The laser generated the P(18) line of the transition $00^\circ 1 \rightarrow 10^\circ 0$, which coincides with the frequency of the ν_3 vibration of $^{11}BCl_3$ molecules. The laser radiation was focused by a NaCl lens (f = 60 mm) into a cell containing the gas. The radiation power intensity at the focus was 2 to 3×10^9 W/cm^2, with the partial mode self-synchronization in a pulse not taken into account. The cell length was 60 mm, the diameter 25 mm. The BCl_3 used contained 98% of basic product and 2% of HCl. The gases O_2, N_2, He, Ne and Ar were dried thoroughly to prevent hydrolysis of BCl_3. The enlarged image of the luminescent area from the quartz side window was incident on the inlet window of the photomultiplier. The diaphragm (D) is used to separate from the luminescent area only the section corresponding to the region of focus where instantaneous dissociation of BCl_3 molecules occurs. When studying the kinetics of BO* formation, the cell was filled with a buffer gas, nitrogen or helium, to a pressure of 20 Torr, so that the retarded collisional dissociation of BCl_3 could be suppressed [3].

Figure 2(a) shows a luminescence pulse in pure BCl_3 (+ 20 Torr He) in the region between 4400 and 6000 Å, which corresponds to the instantaneous stage of BCl_3 molecular dissociation. Under these conditions, the luminescence pulse duration, *i.e.* the time of BCl_3 dissociation, almost coincides with the duration of the CO_2 laser pulse [Fig. 2(b)]. Spectral areas corresponding to luminescence of excited BO* [the transition (1, 1) $^2\Pi_{1/2,\ 3/2} \rightarrow \Sigma^2$, λ_{max} = 4339 - 4365 Å] and BCl* radicals (the transition $A\ ^1\Pi \rightarrow X\ ^1\Sigma^+$, λ_{max} = 2720 Å) were isolated by light filters (F).

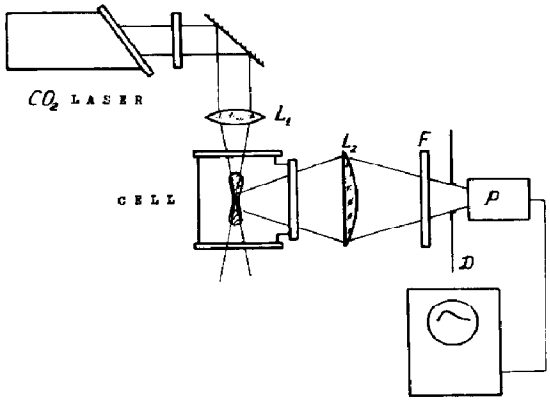


Fig. 1. Scheme of the experimental set-up. L_1, NaCl lens; L_2, quartz lens; D, diaphragm; F, light filter; P, photomultiplier.

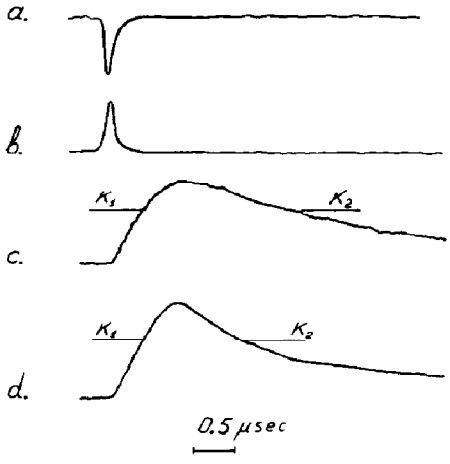


Fig. 2. (a) CO_2 laser pulse; (b) luminescence pulse in pure BCl_3; 4400 Å $\leqslant \lambda \leqslant$ 6000 Å; BCl_3 pressure = 3 Torr, He pressure = 20 Torr; (c) BO* luminescence pulse (BCl_3 pressure = 1.2 Torr, O_2 pressure = 2 Torr); (d) BCl* luminescence pulse, 2700 $\leqslant \lambda \leqslant$ 2800 Å, BCl_3 pressure = 4 Torr.

The characteristic form of BO* and BCl* luminescence pulses is illustrated in Figs. 2(c) and 2(d). The time resolution of the recording system was no worse than 70 ns.

The duration of the rising and failling parts of BO* and BCl* luminescence pulses was measured in the following way. First, the exponential of pulse decay was checked through rear edge logarithmation, and hence the decay rate K_2 was determined. Then the falling part of the pulse extrapolated to the instant $t = 0$, and from this curve the front edge was subtracted. In this manner, the rise of luminescence pulse, K_1, was determined, which turned out to be exponential too.

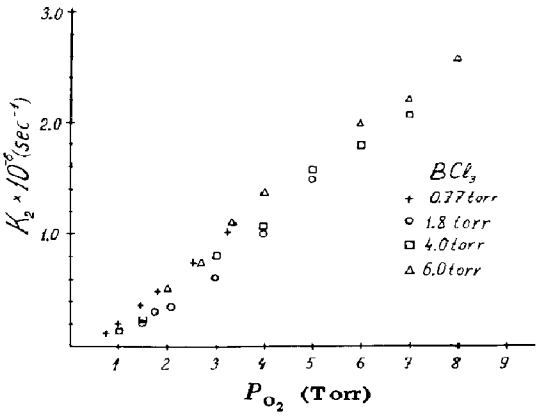


Fig. 3. Dependence of decay rate K_2 of BO* luminescence pulse on oxygen pressure at different pressures of BCl_3.

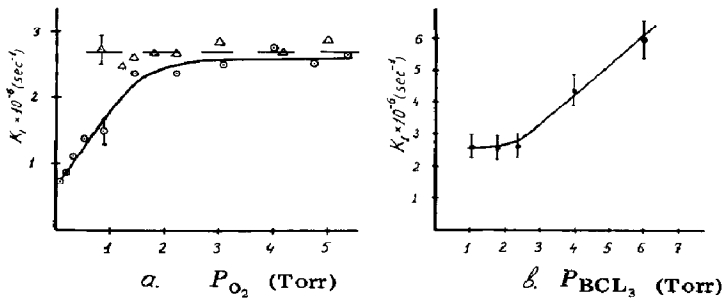


Fig. 4(a). Dependence of rise rate K_1 of BO* luminescence pulse on oxygen pressure at low pressures of BCl_3 (0.27 Torr) (——) and at high pressures of BCl_3 (1.8 Torr) (- - - - -). Fig. 4(b). Rate of BO* pulse rise K_1 aganist BCl_3 pressure.

Results for BO*

The experiments have shown that the luminescence pulse shape of an excited BO* radical depends mainly on oxygen pressure. Therefore we studied the relations between rates K_1 and K_2 (pulse rise and pulse decay respectively) and oxygen pressure at different fixed pressures of BCl_3. The value of K_2 was found to be a linear function of the oxygen pressure P_{O_2} at all the pressures of BCl_3 studied (0.13 - 6 Torr). Figure 3 shows values of K_2 against O_2 pressure with BCl_3 pressures ranging from 0.77 to 6 Torr. Nitrogen was used as a buffer gas, so the total pressure of the mixture in the cell was always 20 Torr. Figure 3 shows that the K_2 decay rate of the BO* luminescence pulse does not depend on BCl_3 pressure, and is governed by oxygen pressure only. From the K_2 *versus* P_{O_2} curve we may estimate the K_2/P_{O_2} value, that is equal to $(4 \pm 1) \times 10^5\ s^{-1}\ Torr^{-1}$. With helium used as a buffer gas, K_2/P_{O_2} is the same value within the limits of experimental error.

The relationship between K_1 and P_{O_2} is more complicated [Fig. 4(a)]. At comparatively high pressures of BCl_3 (1.0 to 6 Torr) and of O_2 (1 to

10 Torr), K_1 is independent of oxygen pressure [the broken line in Fig. 4(a)]. At low pressures of BCl_3 (0.13 to 0.27 Torr), with the oxygen pressure ranging between 0.1 and 1.5 Torr, K_1 increases linearly with oxygen pressure, and with further increase of O_2 the value of K_1 remains constant (the solid line in Fig. 4). Besides, one can observe a dependence of rise rate K_1 on BCl_3 pressure (Fig. 4).

Also, the relationship between K_1, K_2 and buffer gas pressure has been measured with fixed pressures of BCl_3 and O_2. At high pressures of BCl_3 (4 Torr), and of O_2 (2 Torr), both K_1 and K_2 are independent of the buffer gas pressure between 10 and 160 Torr. At low pressures of BCl_3 (0.13 Torr) and O_2 (0.4) Torr K_1 does not depend on buffer gas pressure, while K_2 increases slightly with increase in buffer pressure (Fig. 5).

Discussion of results for BO*

To interpret the results let us consider first a simple model. Under the action of a laser pulse, BCl_3 molecules may dissociate. Since the laser pulse duration T_{las} is shorter than all characteristic time values for the BO* luminescence pulse, we assume that at the instant $t = 0$, some concentration of A radicals is set up very quickly. These radicals interact with oxygen to produce excited BO* radicals. The reactions have the form:

$$A + O_2 \xrightarrow{\alpha} BO^* \tag{1}$$

$$BO^* \xrightarrow{1/\tau} BO + h\nu \tag{2}$$

$$BO^* + M \xrightarrow{\beta} BO \tag{3}$$

where α in eqn. (1) means the rate constant for BO* formation, eqn. (2) is the radiative decay of BO* and τ is the lifetime, eqn. (3) means the collisional deactivation of BO* and β is the rate constant for the process.

On solving the system of eqns. (1) - (3), and neglecting the changes in oxygen concentration during the reaction, we obtain an expression for the dependence of [BO*] on time under the initial conditions $[A]_{t=0} = [A]_0$, $[BO^*]_{t=0} = 0$:

$$[BO^*] = \frac{\alpha[O_2][A]_0}{1/\tau + \beta[M] - \alpha[O_2]} \left\{ e^{-\alpha[O_2]t} - e^{-(1/\tau + \beta[M])t} \right\} \tag{4}$$

Thus, according to this model the shape of the BO* luminescence pulse observed represents the difference of two exponentials. It can also be seen from eqn. (4) that if the exponential indices differ in value, by several times at least, the pulse rise is determined by the exponential with a larger index and the pulse decay by the smaller one. It follows from the model that one of the edges is linearly dependent on oxygen pressure, and the duration of the other cannot be longer than the radiation lifetime τ. The value of τ can be estimated from the data of ref. [18], where τ = 80 - 100 ns. In our

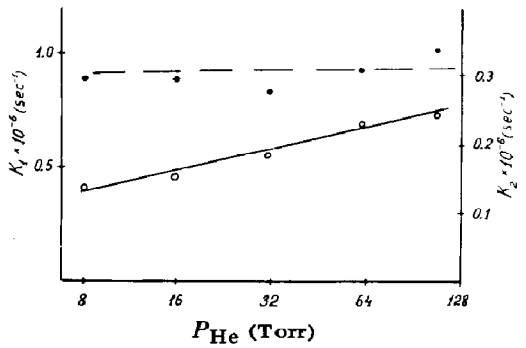


Fig. 5. Dependence of pulse rise rate K_1 (- - - - -) and decay rate K_2 (——) on He pressure. P_{BCl_3} = 0.13 Torr, P_{O_2} = 0.4 Torr.

experiment the duration of the shortest edge is always longer than 100 ns and at low pressures of BCl_3 and O_2 may be as long as 1.3×10^{-6} s.

So the simple model under study, where only the processes of formation of excited BO* radicals and their deactivation are taken into account, offers no explanation of the greater part of the experimental results. We may assume that there is another, intermediate, stage in the formation of excited BO* radicals. The following process may occur as well. The reaction between BCl_3 molecular dissociation products and oxygen gives birth at first to unexcited BO radicals. These then become excited due to collisions with either highly excited BCl_3 molecules or BCl_3 dissociation products. The BO radicals can also participate in further chemical reactions with oxygen, since it is known from ref. [7] that B_2O_3 is the final product of the reaction. The BO* radicals get deactivated during collision or owing to radiation. Hence we have:

$$A + O_2 \xrightarrow{K_2} BO \tag{5}$$

$$BO + M \xrightarrow{K_1} BO^* \tag{6}$$

$$BO + O_2 \xrightarrow{K_3} BO_2 \tag{7}$$

$$BO^* + M' \xrightarrow{K_4} BO \tag{8}$$

where $K_1 = K_1^0\,[BCl_3]$, $K_2 = K_2^0\,[O_2]$, $K_3 = K_3^0\,[O_2]$, $K_4 = 1/\tau + K_4^0\,[M']$. Neglecting the secondary excitation of BO formed in eqn. (8) and solving the equations for reactions (5) - (8), (assuming again that $[O_2]$ = constant), we obtain an expression for [BO*] under the initial conditions $[A]_{t=0} = [A]_0$, $[BO]_{t=0} = 0$, $[BO^*]_{t=0} = 0$:

$$[BO^*] = \frac{[A]_0\,K_1 K_2}{(K_1 + K_3 - K_2)(K_4 - K_2)(K_4 - K_1 - K_3)} \times$$

$$\{(K_4 - K_1 - K_3)\,e^{-K_2 t} + (K_1 + K_3 - K_2)e^{-K_4 t} - (K_4 - K_2)e^{-(K_1 + K_3)t}\} \tag{9}$$

In this case, with a short lifetime of BO* *i.e.* when $K_4 \gg K_2$ and $(K_1 + K_3)$, we may neglect the term with $e^{-K_4 t}$ in eqn. (9) and then get:

$$[BO^*] = \frac{[A]_0 K_1 K_2}{K_4(K_1 + K_3 - K_2)} \{ e^{-K_2 t} - e^{-(K_1 + K_3)t} \} \quad (10)$$

Thus, the pulse shape of BO* luminescence is fully determined now only by the rates of formation and disappearance of BO and by the BO* excitation rate; it *does not depend* on τ.

$K_1^0\ [BCl_3] + K_3^0\ [O_2] > K_2\ [O_2]$

In this case, when the falling part of the BO* luminescence pulse is determined by $K_2 = K_2^0\ [O_2]$, *i.e.* by the rate of BO formation, the decay rate K_2 will always depend linearly on oxygen pressure and is independent on BCl_3 pressure, as observed in our experiment (Fig. 3). Yet in the experiment this relationship does not pass through the origin, but always crosses the abscissa axis (Fig. 3). This may be attributed to the following effect. In the model under consideration we take no account of oxygen concentration variations during the reaction. If we consider this process, still assuming that $\Delta\ [O_2] < ½\ [O_2]_0$, we have $K_2 = K_2^0\ ([O_2] - [A]_0)$. So the K_2–$[O_2]$ relationship must cut a section on the cross axis (Fig. 3) which is equal in magnitude to the pressure of $[A]_0$ (*i.e.* BCl_3 molecular dissociation fragments).

For the BCl_3 pressure of 0.77 Torr this magnitude will be 0.32 Torr, (40% of the BCl_3 pressure). This is in good agreement with the results from ref. [7], where it has been shown that under analogous conditions ~25% BCl_3 molecules can dissociate.

The pulse rise is determined by $K_1 + K_3 = K_1^0\ [BCl_3] + K_3^0\ [O_2]$, *i.e.* by the rates of BO excitation and BO disappearance. With low pressures of BCl_3, when probably $K_1^0\ [BCl_3] < K_3^0\ [O_2]$, the rate of pulse rise K_1 should linearly depend on oxygen pressure. In our experiment, such a dependence is observable at low pressures of BCl_3 and O_2, but with a further increase of oxygen pressure it becomes saturated [Fig. 4(a)]. Besides, in this case, we think an enormously large rate constant K_3^0 is required for the BO + O_2 reaction, which would correspond to 1 or 2 gas kinetic collisions. At high pressures, when the conditions $K_1^0\ [BCl_3] > K_3^0\ [O_2]$ is supposed to be realized, the pulse rise must linearly depend on BCl_3 pressure and not that of oxygen. This is in qualitative agreement with our experimental results [Figs. 4(a) and 4(b)].

$K_2^0\ [O_2] > K_1^0\ [BCl_3] + K_3^0\ [O_2]$

Now the rate of pulse rise K_1 is governed by the reaction rate $K_2^0\ [O_2]$ of BO formation, and the decay rate by those of BO excitation and BO decay $K_1^0\ [BCl_3] + K_3^0\ [O_2]$. In this case, the pulse rise rate should always linearly depend on oxygen pressure, a situation realized experimentally only at low pressures of BCl_3 and O_2 [Fig. 4(a)]. Besides, the signal rise should be independent of BCl_3 pressure, [observed only in experiments with low BCl_3 pressures, [Fig. 4(b)].

The decay rate, determined in this case by $K_1^0 [BCl_3] + K_3^0\ [O_2]$, will linearly depend on O_2 pressure, but this curve will probably always

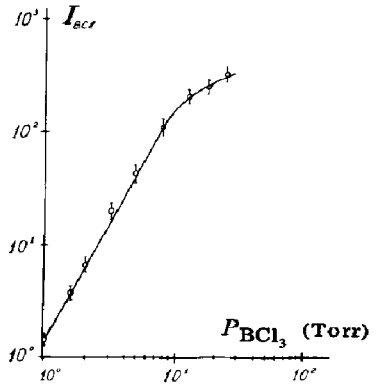


Fig. 6. Dependence of intensity maximum of BCl* luminescence I_m on BCl_3 pressure.

cross the ordinate axis rather than the abscissa axis, as shown in Fig. 4(a).

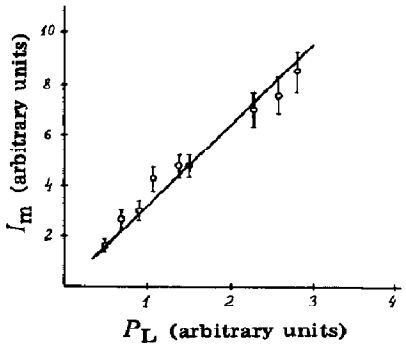
It is clear that in none of the cases can we give a full explanation to the relationships observed in the experiment within the frameworks of the model under study, although in the first case we have better agreement with experiment than in the second case. Nevertheless, using the experimental results available we cannot say definitely what edge, the leading or the trailing, of the BO* luminescence pulse is determined by the reaction rate of BO and BO* formation. Therefore we can estimate only the rate constant of BO or BO* formation. For K_0/P_{O_2} this value is (12 to 4) $\times$ 10^5 s^{-1} $Torr^{-1}$, correspondingly to 8 to 25 gas kinetic collisions. For the AlO radical, the value of the rate constant for its formation in the Al + O_2 reaction corresponds to 10 ± 7 collisions [9].

This model enables us to conclude that excited BO* radicals are probably not a product of the primary reaction between BCl_3 fragments and oxygen. There should be an intermediate stage, that follows excitation of BO radicals; this has been taken into account in the model under study. Excited BO* radicals may also be formed by the reaction of BCl_3 fragments with vibrationally excited O_2. In this case, oxygen excitation is the intermediate stage.

So the absence of short edges in a luminescence pulse, which are associated with the radiative lifetime of BO* radicals, can be explained only if there is an intermediate stage in BO* formation.

Studies of the luminescence kinetics of BCl* radicals

When BCl_3 molecules are dissociated by a high-power i.r. CO_2 laser, apart from a continuous-spectrum luminescence between 4400 and 6000 Å, one can observe intense emission bands of the BCl* radical in the region of 2800 Å, the $A\,^1\Pi \rightarrow X\,^1\Sigma^+$ transition. An important feature is that the BCl* luminescence pulse has no instantaneous phase, *i.e.* BCl* radicals arise not from collisionless dissociation but are formed by the chemical reaction of dissociation products or by collisions of excited BCl_3 molecules.



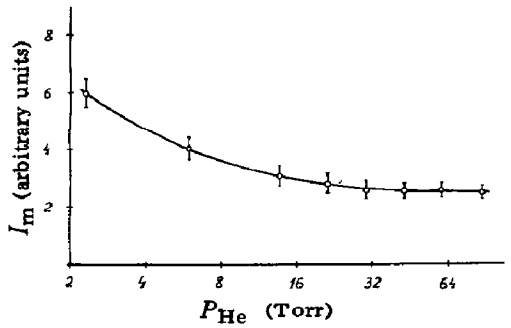


Fig. 7. Dependence of BCl* luminescence intensity (relative units) on laser intensity.

Fig. 8. Dependence of BCl* luminescence intensity (relative units) on He pressure.

The time dependence of BCl* luminescence intensity is analogous to the shape of the signal in the case of BO* (Fig. 2). Figure 6 shows the relation between the maximum of BCl* luminescence intensity, I_m, and BCl_3 pressure. With BCl_3 pressures ranging between 1 and 10 Torr I_m increases quadratically with increase in BCl_3 pressure. Then the increase of I_m slows down, which might be explained by the decrease in the laser radiation power intensity due to absorption in the region before the focus. The quadratic increase of luminescence intensity points to the collisional nature of BCl* formation, which agrees with the absence of the instantaneous phase of BCl* luminescence.

Figure 7 gives the dependence of I_m on laser pulse power. One can see that I_m increases linearly with increase in radiation power.

The relationship between BCl* luminescence intensity and buffer gas (He) pressure has been investigated as well.

Figure 8 shows the dependence of I_m on helium pressure at constant BCl_3 pressure. As the pressure increases, the luminescence intensity drops monotonically and then takes a constant value.

As in the case of BO*, we have studied the dependencies of the rise and decay parts of the BCl* luminescence pulse on BCl_3 and buffer gas pressures. We have found that the rate of pulse rise K_1 and of pulse decay K_2 increase linearly with increase in BCl_3 pressure, both in pure BCl_3 and with the buffer gas present. It turns out that the presence of the buffer gas does not change the duration of either leading or trailing edges: *i.e.*, with P_{BCl_3} = constant, K_1 and K_2 are independent of buffer pressure.

Figure 9 shows the dependencies of K_1 and K_2 on $[BCl_3]$, when helium makes up the constant total pressure of 21 Torr.

The results obtained give for K_1 and K_2:

$$K_1 = 2.0 \times 10^6 + 0.63 \times 10^6 \cdot P_{BCl_3}$$
$$K_2 = 2.5 \times 10^5 + 0.6 \times 10^5 \cdot P_{BCl_3}$$

where K_1 and K_2 are measured in terms of s^{-1} and the BCl_3 pressure P_{BCl_3} in terms of Torr.

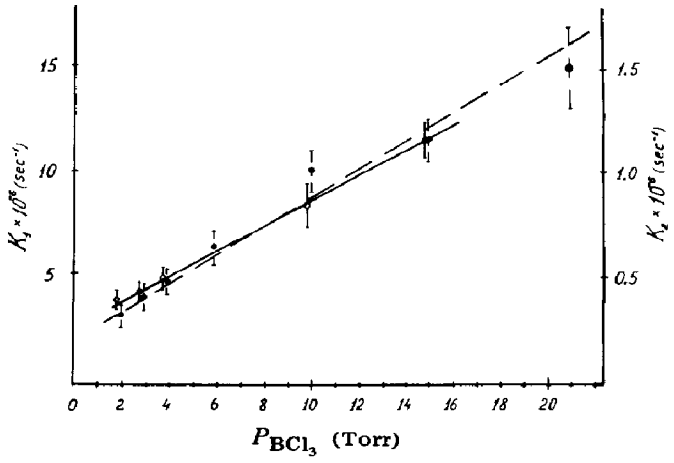


Fig. 9. Dependence of BCl* pulse rise rate K_1 (- - - - -) and decay rate K_2 (——) on BCl_3 pressure.

The mechanism of formation of excited BCl* radicals is similar to that for BO*. In this experiment, as well as in that on BO* luminescence, we have not observed short edges corresponding to the radiative decay of BCl* with the lifetime of its $A\,^1\Pi$ state (19 ns [8]); as in the case of BO*, excited BCl* radicals are formed by secondary processes, *e.g.*, when BCl radicals undergo excitation.

For now, the experimental data available do not enable us to conclude what particular processes result in BCl* radicals, and to which of them the front and rear edges of BCl* luminescence correspond. We can only say that excited BCl* is formed by collisions in an intensive field, but not by collisionless dissociation of BCl_3. The quadratic dependence of luminescence intensity and the linear dependence of K_1 and K_2 on BCl_3 pressure, as well as the decrease in luminescence intensity as a buffer gas is added proof for this.

Conclusion

The results obtained illustrate the potentialities of i.r. photolysis of polyatomic molecules in the strong field of a CO_2 laser: a new method of radical production. This quite simple method makes it possible to achieve considerable radical concentrations down to the lowest pressures, ~0.03 Torr, during a short time interval practically determined by the laser pulse duration. This, in its turn, provides a means for studying the process of high-rate radical reactions, as has been done in the present work on BO* formation.

The use of u.v. and visible tunable lasers in observing the concentration of unexcited radicals [10] may be the next step in the development of the method of i.r. photolysis of molecules. This will enable us to obtain information on such radical reactions which are difficult or even impossible to study by the methods currently available.

Acknowledgements

The authors wish to thank their colleagues Professor Dr. R. V. Ambartzumian and Dr. A. A. Makarov for helpful discussions.

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