MAGNETIC FIELD EFFECTS ON THE GAS-PHASE PHOTOLYSIS OF NITROGEN DIOXIDE: PRESSURE DEPENDENCE OF THE PHOTOLYSIS RATE

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Magnetic field effects on the NO_2 photolysis rate at an energy range below the dissociation threshold are shown to be identical to those observed in fluorescence. According to the data obtained, both the $^2B_2$ and $^2B_1$ states of NO_2 are reactive. The high pressure data have been explained in terms of an excited collision complex $(NO_2)_2^*$, which is efficiently quenched by collisions.

1. Introduction

The study of electronically excited NO_2 is of considerable interest in understanding the mechanisms for radiationless relaxation of electronic excitation energy in small molecules.

Whatever the excitation energy, photolysis of NO_2 is known [1–6] to give NO and O_2. If the excitation energy is in the photodissociation region of NO_2, decomposition into NO and the $O(^3P)$ atom is the primary photochemical process [1–6]. The reaction of O with NO_2 in secondary processes yields NO and O_2. The quantum yield for photochemical dissociation of NO_2 measured by the yield of O_2 within the energy range under study is 1 [4,5].

A strong dependence of the photolysis quantum yield on the excitation wavelength is observed for excitation of NO_2 below the dissociation threshold [4,5]. A detailed study of the photolysis mechanism within this energy range is not available. In particular, the role of electronically excited states of NO_2 in photolysis and the nature of the primary photochemical process are not clear.

The question as to the role of electronically excited states of SO_2 and CS_2 in their photochemical processes has been solved by comparing data on the magnetic field effect on both the fluorescence and the photolysis rate of SO_2–*n*-pentane mixtures [7,8], and by a similar comparison with pure carbon disulfide [9,10].

A similar procedure is suitable for NO_2 since this molecule's fluorescence exhibits quenching magnetic effects [11–13]. The magnetic field has been shown to influence only the discrete structure of the fluorescence spectrum associated with the radiative transition $^2B_1 \rightarrow {}^2A_1$ [11–13]. The magnetic field does not affect the structureless broad band in the NO_2 fluorescence spectrum. It is assumed that this band is caused by transitions from the $^2B_2$-state rovibronic levels strongly related to the high-lying levels of the $^2A_1$ ground state via electron-oscillation interactions [14]. Although the mechanism of the magneto-induced NO_2 fluorescence quenching is not studied in detail, the above data may be used to solve the problem as to the role the electronically excited $^2B_1$ and $^2B_2$ states in photolysis.

The second important problem is the determination of the primary photochemical process. Indirect information may be obtained by studying the dependence of the NO_2 photolysis rate on pressure.

Hence, the aim of the present Letter is to study the magnetic field effect on the NO_2 photolysis rate and to compare these results with the data in refs. [11–13]. The paper is also concerned with NO_2 photolysis at different excitation energies over a wide range of NO_2 pressures.

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2. Experimental

The experimental equipment is described in detail elsewhere [7–10,15].

The maximum degree of conversion of NO_2 in our experiments was below 1%.

The nitrogen dioxide was synthesized as described in ref. [16] with a subsequent vacuum distillation at $T = 36\,^{\circ}C$ (the N_2O_4 pressure at this temperature was of the order of 10 Torr [17]).

Nitrogen dioxide is known to be in equilibrium with its dimer [19]:

$$2NO_2 \rightleftharpoons N_2O_4 . \qquad (1)$$

The equilibrium constant of process (1) at $T = 27\,^{\circ}C$ is 8×10^{-3} Torr [19] (the experimental temperature was 27–29°C). The N_2O_4 pressure at total gas pressure of 30 Torr, was 4.9 Torr.

The N_2O_4 absorption cross section in the $\lambda \geqslant 3900$ Å spectrum range is negligible, and at $\lambda = 3650$ Å is 3×10^{-3} $Torr^{-1}$ cm^{-1} [20]. The NO_2 cross section is $(6.5\text{–}7.0)\times10^{-3}$ $Torr^{-1}$ cm^{-1} [20]. Thus the dimer absorption is an order of magnitude lower than the NO_2 absorption at $\lambda = 3650$ Å. We have neglected effects associated with the photochemical dimer decomposition since they do not exceed 10%.

Let us consider the quenching of excited NO_2 molecules by N_2O_4 molecules and the shift in equilibrium (1) during the course of the photolysis. The equilibrium shifts to the left due to NO_2 decomposition. As the photolysis rate is measured from the decrease in gas pressure, these effects may influence the photolysis rate obtained. The corrections due to these effects do not exceed 6% [21]. This value is well within our experimental error.

3. Experimental results

Fig. 1 shows the pressure dependence of the NO_2 photolysis rate for various excitation energies. The same figure presents data [6] (curve 4) for NO_2 photolysis by an argon laser ($\lambda = 4880$ Å). A fair agreement is observed.

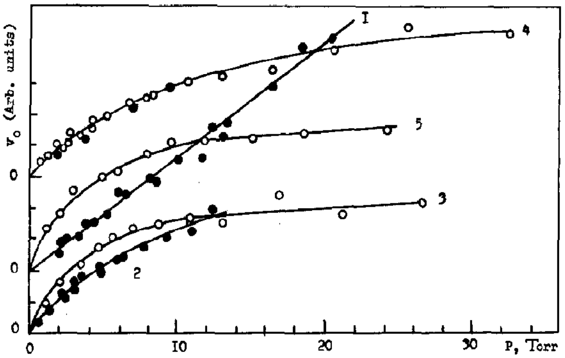

Fig. 1. Pressure dependence of the NO_2 photolysis rate for different excitation wavelengths: (1) 3650 Å, (2) 4350 Å, (3) 5460 Å, (4) $\geqslant$4500 Å, (5) $\geqslant$5880 Å. The curves are scaled to have the same amplitude. Full circles are the data for $\lambda \geqslant 4500$ Å [6].

These data show that on excitation above the dissociation threshold ($\lambda = 3650$ Å) the NO_2 photolysis rate increases linearly with gas pressure while for excitation below the dissociation threshold ($\lambda \geqslant 3980$ Å) the dependence is non-linear.

Fig. 2 contains the $R = P/v_0$ versus P dependences for two excitation energies. Here P is the gas pressure and v_0 is the photolysis rate in the absence of the magnetic field. These dependences are linear (this is true for all excitation energies). The relation between the slope and intercept q is 0–$\lambda_{exc} = 3650$ Å; (0.08 ± 0.01)–$\lambda_{exc} = 4350$ Å; (0.10 ± 0.01)–$\lambda_{exc} \geqslant 4500$ Å; (0.29 ± 0.01)–$\lambda_{exc} = 5460$ Å; (0.34 ± 0.02) –$\lambda_{exc} \geqslant 5880$ Å. With increasing excitation energy this value decreases.

We now consider the magnetic field effect on the NO_2 photolysis rate. In these experiments the gas pressure is varied within the range 1.1–30.0 Torr. It has been shown that within experimental error the magnetic field effect in the reaction is independent of pressure and at the magnetic field strength of 8.4 kG is $(0.85\pm0.03)v_0$. As shown in refs. [11–13] the

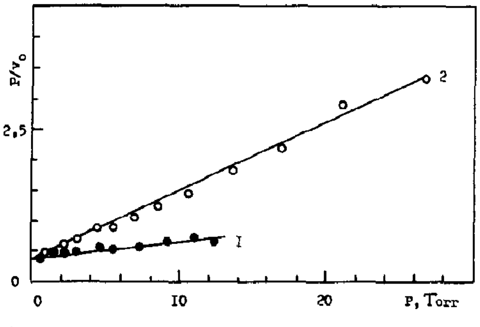

Fig. 2. Pressure dependence for $\lambda_{ex} = 4350$ Å (1) and $\lambda_{ex} = 5460$ Å (2).

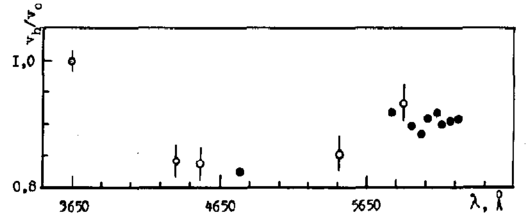

Fig. 3. Magnetic field effects on the exciting wavelength dependence at an NO_2 pressure of 5.5 Torr in a magnetic field of 8.4 kG. Full circles show the data from ref. [13], on magnetically induced quenching of the NO_2 fluorescence.

magnetic field effect in fluorescence is also pressure independent in the pressure range considered.

Fig. 3 shows the dependence of the magnetic field effect on the excitation energy for a gas pressure of 5.5 Torr and a magnetic field strength of 8.4 kG. Also shown are the results on the NO_2 fluorescence quenching in the magnetic field [11–13]. A satisfactory agreement between the fluorescence and photochemical measurements is observed. Note that at 3650 Å excitation (above the dissociation threshold) there is no magnetic field effect on the photolysis rate.

Fig. 4 shows the dependence of the magnetic field effect in NO_2 photolysis on the magnetic field strength at a pressure of 2 Torr and an excitation wavelength above 4500 Å. Also shown are the results of the magnetic field effect on the NO_2 fluorescence [13] excited by the argon laser ($\lambda = 4880$ Å), at a gas pressure of 0.59 Torr. Good agreement between the results of photochemical and fluorescence measurements is observed.

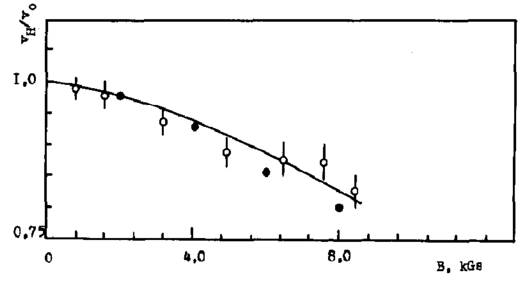

Fig. 4. Magnetic field effects on the field strength dependence at an NO_2 pressure of 2.1 Torr in the spectral range $\lambda \geqslant 4500$ Å. Full circles show the data from ref. [13] on NO_2 fluorescence quenching in a magnetic field at $\lambda_{ex} = 4880$ Å. The pressure is 0.59 Torr.

4. Discussion

Let us first consider NO_2 photolysis in the absence of the magnetic field. Our experimental results cannot be described in terms of the simple kinetic scheme given in ref. [6]. According to this scheme, the photolysis rate must increase linearly with gas pressure. Such behaviour for the NO_2 photolysis rate is only observed at excitation energies exceeding the dissociation threshold ($\lambda_{exc} = 3650$ Å). When the excitation energy is below this threshold, substantial deviations from linearity take place (see fig. 1).

An unambiguous description of these deviations may be given within the framework of the model described in refs. [21–24], and in ref. [10]. In accordance with this model, it is believed that the collision between excited and ground state NO_2 molecules may yield an excited complex (excimer) $(NO_2)_2^*$ that can decompose unimolecularly by three channels: formation of NO_2^* and NO_2, formation of $2NO_2$ (quenching) or formation of the primary photolysis products (presumably, NO and NO_3). Additionally the $(NO_2)_2^*$ complex may be quenched by collisions with ground state NO_2 molecules.

According to this model, the rate should depend on the biomolecular rate constant for $(NO_2)_2^*$ complex quenching (k_8) and the sum of the rate constant for unimolecular complex decomposition via the first channel with some weight (αk_5) and the constants for unimolecular complex decomposition by the second and third channels ($k_6 + k_7$) [21]. Here the value of α is determined from the ratio of the bimolecular rate constant for NO_2^* quenching by NO_2 (k_3) to the sum of the bimolecular rate constant for the quenching k_3 and the constant for $(NO_2)_2^*$ complex formation (k_4), i.e. $\alpha = k_3/(k_3 + k_4)$ [21].

Thus, $q = k_8/(\alpha k_5 + k_6 + k_7)$ and assuming k_8 to be of the order of the gas-kinetic constant ($\approx 10^7$ $Torr^{-1}$ s^{-1}) one may estimate the upper limit for the excited complex lifetime. These estimates for the upper limit of the $(NO_2)_2^*$ lifetime yield values lying in the range 8.0–34.0 ns. The real complex lifetime may be substantially smaller since we estimate the value $(\alpha k_5 + k_6 + k_7)^{-1}$ in which $\alpha < 1$, and the $(NO_2)_2^*$ lifetime is defined by the value $(k_5 + k_6 + k_7)^{-1}$.

Similar deviations in the Stern–Volmer dependences for the fluorescence quenching have been observed for SO_2 [25], CS_2 [10], NO_2 [26] and N_2

[22]. In photolysis these deviations have been detected for formaldehyde [23] and mixtures of SO_2 with *n*-pentane [24].

The above deviations have been described in terms of a similar model [10,21–24]. In the model in refs. [25, 26] excitation takes place to the A* state of NO_2, while fluorescence is observed from the A** state.

The A*→A** transition is assumed to be unimolecular. A detailed analysis [21] shows this model to be in contradiction with a series of experimental facts and theoretical notions.

To account for the observed dependences of the NO_2 photolysis rate on pressure, it is assumed that the initial photochemical process is a unimolecular decomposition of the excited complex $(NO_2)_2^*$ into NO and NO_3. Secondary processes lead to formation of NO and O_2. The excited $(NO_2)_2^*$ lifetime depends on the excitation wavelength and its upper limit is 8.0–34.0 ns.

We now discuss the results for the magnetic field effect on the NO_2 photolysis rate.

As mentioned above, the discrete structure in the NO_2 fluorescence spectrum is quenched in the magnetic field. The discrete structure is associated with the electronic transition $^2B_1 \rightarrow {}^2A_1$ [11–13]. As shown (figs. 3 and 4), data on the magneto-induced NO_2 fluorescence quenching agree, to a high accurcy, with those for NO_2 photolysis in the magnetic field. Thus, with excitation at wavelengths above 3980 Å, both electronic states, $^2B_1$ and $^2B_2$, are reaction states in the NO_2 molecule. Alternatively, the dependences of the magneto-induced fluorescence quenching and the magnetic field effect on the photolysis rate would be substantially different.

The integral intensity of the discrete fluorescence spectrum amounts to 20% of the total NO_2 fluorescence intensity [13]. Thus from fig. 4 it may be concluded that the $^2B_1$ state contribution to the photolysis rate is of the order of 20%, and that of the $^2B_2$ state is 80%.

Finally, on the basis of the results of the magnetic field effect on the NO_2 photolysis rate it is concluded that the reaction states in the NO_2 molecule are the $^2B_1$ and $^2B_2$ electronic states, which are independently populated.

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