Dual Photon Effects in Nitrogen Dioxide Photolysis

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The photolysis of NO$_2$ has been studied using the pulsed ruby laser. As reported earlier the NO and O$_2$ is formed where the energy of the photons of wavelength 6943 Å corresponds to 41.2 kcal, while the dissociation energy of NO$_2$ (to NO + O atom) corresponds to 71.8 kcal. The process required the assumption of energy pooling of some type and the consecutive absorption of two photons was postulated. The production of oxygen by NO$_2$ photolysis was anticipated to be dependent on the square of the intensity of the laser pulse. Results reported here confirm this relationship over a range of intensity from 2×10^{18} to 6×10^{18} photons per pulse. Fluorescence around 4000 Å is observed which is of short duration with intensity and lifetime dependent on pressure. At constant pressure the intensity of fluorescence is also approximately dependent on the square of the intensity of the laser pulse. The fraction of fluorescence emission is estimated to be less than 10^{-11} of the laser pulse intensity.

Introduction

A previous study done in this laboratory demonstrated two-photon consecutive absorption as being the most probable mechanism for the photodissociation of NO$_2$ using a pulsed ruby laser at 6943 Å.[1] Additional data reported here confirmed this and also examined associated phenomenon, that of multiphoton induced fluorescence.

The dissociation of NO$_2$ by ON-O bond cleavage requires 3.14 eV, while the laser energy corresponds to 1.785 eV.[2] The pooling of the energy of two photons would give more than enough energy to dissociate the NO$_2$ into NO + O.

Several mechanisms including one, simultaneous absorption of two photons; two, reaction of two singly excited NO$_2$; three, reaction of a singly excited NO$_2$ with a ground state NO$_2$; and four, consecutive absorption of two photons were examined. All but the last, the consecutive absorption of two photons (mechanism four), were eliminated since for mechanism one, there would have been too low a yield of O$_2$ to otherwise account for the observed product; for two, an (NO$_2$) pressure squared dependence would have been expected whereas a first-order dependence on (NO$_2$) was observed at lower pressures and the yield of O$_2$ would have been lower than that observed; and for three, although energetically possible this third mechanism has never been observed as would be expected in other normal photolysis experiments of NO$_2$ with wavelength above the dissociation limit.

In earlier experiments direct evidence that the reaction was second order with respect to laser intensity had not been observed. This evidence along with the observation of a fluorescence in the blue region of the spectrum was found and is reported below.

Experimental Section

The same Korad K-1 laser system was used as before except that the cryptocyanine dye passive Q switch had been replaced by an electronic Q switch providing much greater reproducibility and nearly eliminating all problems with multiple pulsing. Energy of the laser output was found to be 2.28 J (or 8×10^{18} photons/pulse) with a half width duration of 10 nsec.

Laser intensity was varied by firing the laser through optically flat Pyrex plates held at set angles in slotted aluminum channeling mounted on an optical rail. This apparatus was calibrated using a Spectra-Physics continuous mode He–Ne laser, monitoring the transmitted intensity with a filtered RCA 1P21 photomultiplier.

The O$_2$ formed was analyzed using a CEC 21-130 mass spectrometer. The sample was flowed through a U-tube at liquid nitrogen temperature before entering the mass spectrometer. All the NO$_2$ was frozen out on the walls, and the O$_2$ and Ar were measured without interference at m/e 32 from the ^{14}N^{18}O$^+$ peak which ordinarily would make impossible measurement of small amounts of O$_2$ in NO$_2$. Back reaction of O$_2$ with either NO or solid N$_2$O$_3$ was estimated to be negligible under the conditions used in the time period from start of photolysis to end of analysis (20 min). The fluorescent emission was observed using an RCA 8575 photomultiplier, following the decay on a Tektronix 7904 oscilloscope and photographing the trace with the C51 camera unit. The fluorescence unit was of conventional arrangement with the important exception of the roles of the primary and secondary filters being reversed. Therefore the exciting light beam passed through a cutoff filter with wavelengths above the cutoff wavelengths being transmitted and the fluorescent light was passed through a filter combination with a window of 3700–4400 Å, wavelength much smaller than the exciting beam. The filters used for excitation were two Corning CS2-64; for emission they were two Corning CS4-72, a Corning CS5-57, and a Kodak Wratten 38A.

Gases were handled as mentioned previously, and the equilibrium constants of Harris and Churney were used for correcting the pressure of NO$_2$ for the NO$_2$–N$_2$O$_4$ equilibrium.[3] The gas mixture was $^2/_3$(NO$_2$ + N$_2$O$_4$) and $^1/_3$ Ar.

Results

The results were obtained using two methods of analysis. The O$_2$ produced by NO$_2$ photolysis was analyzed using the mass spectrometer. By varying the laser intensity we measured O$_2$ produced as a function of laser intensity, I_L. A log-log plot (Figure 1) of O$_2$ vs. I_L gives a
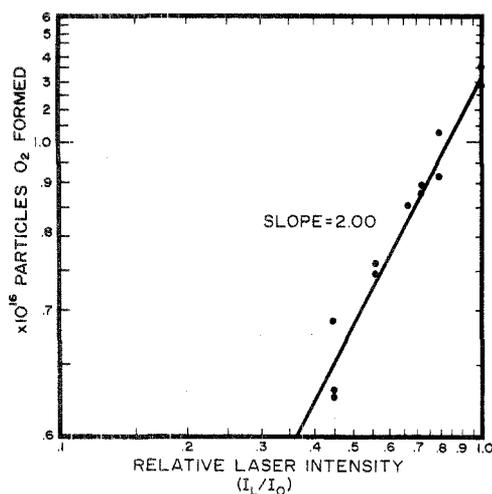
Figure 1.

Figure 2.

Figure 3.

straight line with a least-squares slope of 2.00 (σ = ±0.053).[4] This was done at a constant total pressure of 23.2 Torr, corresponding to (NO_2) = 14 Torr.

A weak emission of light in the range of 3700–4440 Å from the flask irradiated with the laser light was observed and the integrated fluorescent intensity, I_F, measured by photographing the oscilloscope display. The log–log plot (Figure 2) of I_F vs. I_L gave a straight line of least-squares slope 2.45 (σ = ±0.063). The total pressure used for these measurements was 65.1 Torr, corresponding to (NO_2) = 32 Torr. The higher pressure was used to obtain sufficient intensities to perform the log–log plot, since the efficiency of fluorescence was very low. At this point it can be noted that the scatter in the data is within the estimated limits of instrumental and experimental error; it is fairly difficult to perform these measurements with greater accuracy. This emission was observed through filters in a wavelength band of 3700–4400 Å.

A plot of I_F vs. (NO_2) was also done (Figure 3) and shows that an intensity maximum is reached around (NO_2) = 40 Torr. The observed lifetimes varied from 40 to 140 nsec over the pressure range studied, with lifetime inversely proportional to pressure.

Discussion

The results of the laser experiments determining oxygen produced at various intensities of the laser were given in the log–log plot (Figure 1). The slope of the least-squares line through these points was 2.0, or the oxygen produced was proportional to the square of the intensity of the laser pulse. That we get an experimental value of 2.0 for O_2 production confirms the previous indication of two-photon consecutive absorption taking place, the mechanism being given by

$$NO_2 + h\nu_L \xrightarrow{\gamma_1} NO_2{}^*$$

$$NO_2{}^* + h\nu_L \xrightarrow{\gamma_2} (NO_2{}^{**}) \longrightarrow NO + O$$

$$NO_2{}^* + M \xrightarrow{\lambda} NO_2 + M$$
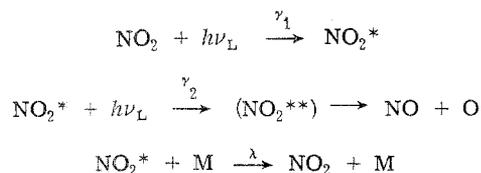
Here M can be any quenching species and λ is the pseudo-first-order quenching constant where λ = $k_Q(M)$ and (M) is assumed to be constant.[1] This is rapidly followed by

$$NO_2 + O \longrightarrow NO + O_2$$
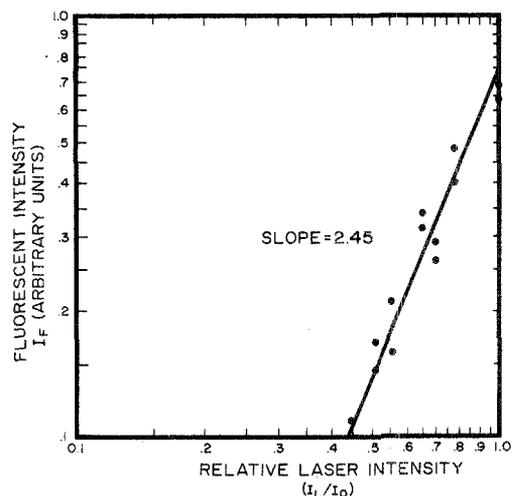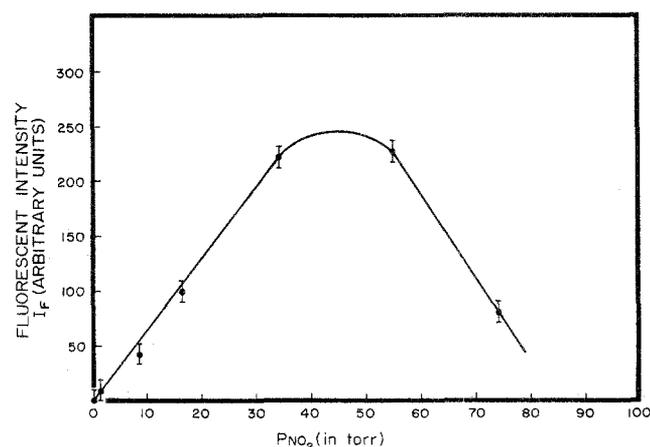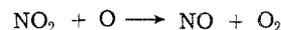
The short-lived intermediate $NO_2{}^{**}$ will be quenched very little at the pressures of interest, however, quenching of the $NO_2{}^*$ during the 10^{-8} sec pulse duration must be considered for an accurate appraisal of the situation. An equation describing the amount of O_2 produced has been previously developed using the three rate equations for the mechanism above.

$$+ \; d(NO_2{}^*)/dt = \gamma_1(NO_2)$$

$$+ \; d(O_2)/dt = \gamma_2(NO_2)$$

$$- \; d(NO_2{}^*)/dt = [\gamma_2 + \lambda](NO_2{}^*)$$

and assuming that (NO_2) is essentially constant in time (which it is under the experimental conditions used, less than 1% of the NO_2 being excited).

$$(O_2) = \frac{\gamma_1\gamma_2(NO_2)I}{(\gamma_2 + \lambda_1 + \lambda_2 + \ldots)} \times$$
$$\left[1 + \frac{e^{-(\gamma_2 + \lambda_1 + \lambda_2 + \cdots)T} - 1}{(\gamma_2 + \lambda_1 + \lambda_2 + \ldots)T} \right]$$

Letting quenching of $NO_2{}^*$ equal to zero gives the relation

$$(O_2) = \gamma_1(NO_2)T \left[1 + \frac{e^{-\gamma_2 T} - 1}{\gamma_2 T} \right]$$

Using a power series expansion for e^{-x} and keeping the first three terms gives the simplified equation for the low-pressure limit description of O$_2$ formation

$$(O_2) = \gamma_1 \gamma_2 (NO_2) T^2 / 2$$

where $\gamma_1 = I_L \alpha_1$, $\alpha_1 \cong 0.15$ cm^{-1} atm^{-1};[5] $\gamma_2 = I_L \alpha_2$, $\alpha_2 \cong 3.5$ cm^{-1} atm^{-1};[1] $T =$ time of laser pulse $= 10^{-8}$ sec; (NO$_2$) = pressure of NO$_2$. This predicts an I_L dependence on O$_2$ production as was found.

One possible phenomena was that of the energy of two photons "pooling" in some manner that would allow emission of radiation with wavelengths smaller than that of the laser to be observed. A very weak emission was observed and demonstrated a two-photon dependence as indicated by the log–log plot of I_F vs. I_L.[6]

The quantum efficiency, ϕ_f, was estimated for the process

$$NO_2^{**} \longrightarrow NO_2 + h\nu_F$$

where $\nu_F > \nu_L$, ν_F = frequency of fluorescent light, ν_L = frequency of laser light, and the quantum efficiency is defined as

$$\phi_F = \frac{\text{no. of } h\nu_F \text{ observed}}{\text{no. of possible } NO_2^{**} \text{ formed}}$$

The number of NO$_2^{**}$ formed is estimated from the relation describing oxygen formation, assuming that every NO$_2^{**}$ dissociates and one O$_2$ is formed. The number of photons is estimated by integrating the signal with respect to time to get the total signal in coulombs, then dividing this by the gain of the photomultiplier tube, the quantum efficiency of the tube in that wavelength region, and the transmittance of the filter combination and finally by multiplying by 1.602×10^{19} (the number of electrons/coulomb) and by $\sim 3 \times 10^3$ which is the estimated geometric factor assuming inverse square dimunition of the light intensity and assuming no effective diffusion of fluorescing species from the beam path. This leads to a value of $\phi_f \sim 6 \times 10^{-9}$ or less than 10^{-11} of the laser pulse is converted to fluorescent light.

The collision-free radiative lifetime of NO$_2^*$ below its dissociation limit is about 5×10^{-6} sec.[7,8] Since an NO$_2^{**}$ above its dissociation limit, probably in the $^2B_2$ upper electronic state, will live for a lifetime of approximately 2×10^{-13} sec,[9,10] one might expect a quantum efficiency for fluorescence on the order of $(2 \times 10^{-13}/5 \times 10^{-6} \sim 4 \times 10^{-8})$. The estimated experimental quantum efficiency is therefore in the neighborhood of one-tenth of that predicted. Characteristic of this emission would be its very short lifetime since no NO$_2^{**}$ will last longer than the time of a few vibrations. The experimentally determined relatively long lifetimes of 4×10^{-8} to 1.4×10^{-7} sec indicate that the NO$_2^{**}$ is quenched prior to emission or that NO$_2^*$ is vibrationally quenched before absorbing the second photon. These lifetimes are compatible with the collision-limited lifetimes calculated using the known quenching constants of Myers, Silver, and Kaufman.[11] Using values from the literature for the vibrational energy of NO$_2^*$ one sees that some combination of three–four vibrational quanta must be lost to yield an NO$_2^*$ that will have the radiative lifetime observed.[7,8] This fact coupled with the knowledge that an NO$_2^*$ during the 10^{-8} sec laser pulse will undergo $\sim 5 \times 10^4$ times as many collisions as an NO$_2^{**}$ during its 2×10^{-13} sec lifetime leads one to conclude that the mechanism for the dual-photon-induced fluorescence in the spectral region observed must be

$$NO_2 + h\nu_L \longrightarrow NO_2^*$$
$$NO_2^* + M \longrightarrow NO_2' + M$$
$$NO_2' + h\nu_L \longrightarrow NO_2''$$
$$NO_2'' \longrightarrow NO_2 + h\nu_F$$
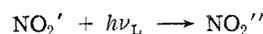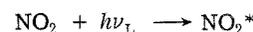
with $\nu_D > \nu_F > \nu_L$ and where NO$_2'$ is somewhat vibrationally deactivated, but still in the $^2B_1$ electronically excited state, and ν_D is the frequency of light necessary to dissociate NO$_2$. That the fluorescence process reached its peak at a much higher pressure than the O$_2$ formation is indicative of the role quenching has in enhancing this phenomena.

The marked decrease in I_F with increasing pressure after reaching its maximum value may be attributed to the increasing concentration of N$_2$O$_4$ present at higher pressures. The N$_2$O$_4$ apparently has a very high efficiency for quenching the $^2B_1$ state to the ground level. Also, N$_2$O$_4$ may have an added effect in this scheme since the reaction

$$NO_2^{**} + N_2O_4 \longrightarrow NO_2' + 2NO_2$$

may yield an electronically excited NO$_2$ lower in energy by at least the strength of the O$_2$N–NO$_2$ bond (about 13.0 kcal/mol).[12] This brings the excitation energy below the dissociation limit with one collision and may be one reason that the two-photon process peaks at a higher pressure than O$_2$ production.

No short-lived fluorescence was observed, as might have been expected from NO$_2^*$ with excitation energy greater than the dissociation. This is not to imply that this and other photon effects were not occurring, but simply were not detectable using our present experimental apparatus. Nevertheless, this technique, for example, did allow the observation of a rare photochemical phenomena without a great deal of interference from the laser beam since the observations were performed at wavelengths both far from the laser line and of much greater energy than the laser line.

In summary we can write a general mechanism for processes induced by the laser photolysis of NO$_2$ as follows

$$NO_2 + h\nu_1 \longrightarrow NO_2^*$$

$$NO_2^* + \begin{cases} M \longrightarrow NO_2 + M \\ M \longrightarrow NO_2' + M \\ h\nu_2 \longrightarrow NO_2^{**} \end{cases}$$

$$NO_2^{**} \begin{cases} \longrightarrow NO(^2\Pi) + O(^3P) \\ + M \longrightarrow NO_2'' + M \end{cases}$$

$$O + NO_2 \longrightarrow NO + O_2$$
$$NO_2' + h\nu_2 \longrightarrow NO_2''$$
$$NO_2'' \longrightarrow NO_2 + h\nu_F$$
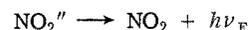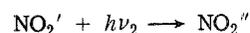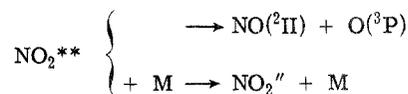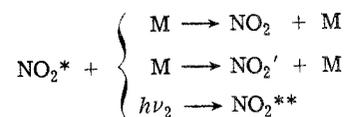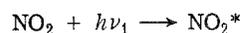
where NO$_2^*$, NO$_2'$, and NO$_2''$ are all $^2B_1$ excited states but differ in vibrational energy, and NO$_2^{**}$ is in the $^2B_2$ state. For reactions where competition can take place the relative rates are determined by laser intensity and pressure. Under our conditions about 20% of the NO$_2^*$ react to form O$_2$.

Further work on the spectral distribution of this fluorescence and the effects of quenching (for example, Kr $vs.$ CO_2 and particularly that of N_2O_4) on enhancing one pathway over the other is underway.

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References and Notes

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Cross Disproportionation of Alkyl Radicals

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The cross disproportionation of several alkyl radicals has been measured using a novel technique that eliminates most of the uncertainties characterizing previous gas-phase results. The radicals are prepared in the condensed phase at 90 K by the H atom addition to a mixture of two olefins. The concentrations are adjusted so that one of the two radicals produced is in great excess. The other radical, then, is involved only in cross and not in autodisproportionation. From the results of a number of measurements, it is shown that alkyl radical disproportionation is governed almost completely by steric factors whereby the hydrogen acceptor–donor characteristics of each radical of the cross-disproportionating pair are independent of the counter radical. The cross disproportionation of an alkyl radical containing a double bond shows that the double bond has an orienting effect on the approach to and reaction with a second radical.

Alkyl radicals are intermediates in many reactions such as alkane pyrolysis, hydrogen atom addition to olefins, and photolysis and pyrolysis of appropriate carbonyls. The elementary reaction steps in the reaction of two alkyl radicals are combination and disproportionation. As an illustration, the reactions between the two radicals, *tert*-butyl and *sec*-butyl are

$$CH_3\!-\!\overset{\cdot}{\underset{\underset{\textstyle CH_3}{|}}{C}}\!-\!CH_3 \; + \; CH_3\!-\!CH_2\!-\!\overset{\cdot}{C}H\!-\!CH_3 \longrightarrow$$

$$CH_3\!-\!\overset{\underset{\textstyle}{\overset{\textstyle CH_3}{|}}}{\underset{\underset{\textstyle CH_3}{|}}{C}}\!-\!\overset{\overset{\textstyle}{}}{\underset{\underset{\textstyle CH_3}{\diagdown}}{C}}H\!-\!CH_2\!-\!CH_3 \qquad (A)$$

$$CH_2\!\!=\!\!\overset{}{\underset{\underset{\textstyle CH_3}{|}}{C}}\!-\!CH_3 \; + \; CH_3\!-\!CH_2\!-\!CH_2\!-\!CH_3 \qquad (B)$$

$$CH_3\overset{}{\underset{\underset{\textstyle CH_3}{|}}{C}}H\!-\!CH_3 \; + \; CH_3\!-\!CH_2\!-\!CH\!\!=\!\!CH_2 \qquad (C)$$

$$CH_3\overset{}{\underset{\underset{\textstyle CH_3}{|}}{C}}H\!-\!CH_3 \; + \; CH_3\!-\!CH\!\!=\!\!CH\!-\!CH_3$$
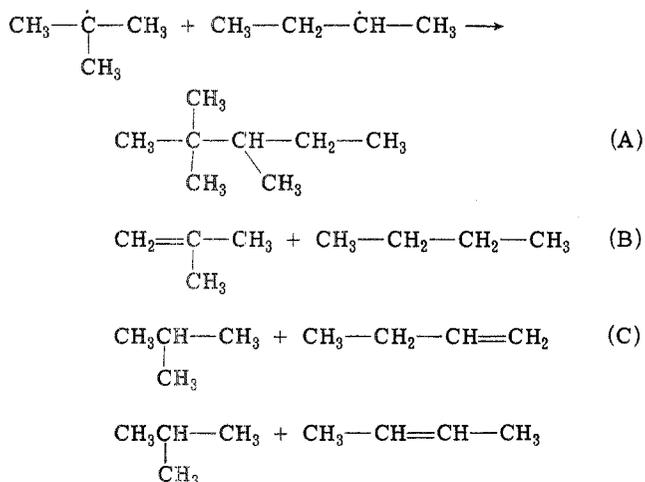
The combination reaction is given by A. In the disproportionation reaction B, the *tert*-butyl acts as hydrogen donor, and the 2-butyl radical as acceptor. There are nine "available" and equivalent primary hydrogens in the *tert*-butyl radical, all leading to isobutylene. The donor radical in C is 2-butyl. The transfer of a primary hydrogen leads to 1-butene and that of either of the two secondary hydrogens gives 2-butene. The hydrogen transfer is accompanied by olefinic bond formation. Only hydrogens on the carbon adjacent to the carbon with the unpaired electron are transferable.

The disproportionation–combination ratios for a number of straight as well as branched chain alkyl radical pairs have been measured and reviewed.[1] It has been suggested that the k_d/k_c ratio is strongly related to the number of transferable hydrogens. Kraus and Calvert,[2] in observations on butyl radicals (t-C_4H_9, i-C_4H_9, and s-C_4H_9), reported an excellent correlation for various butyl radicals on this basis if it is assumed that the specific rates for combination are equal for all radical pairs. Bradley, in his discussion of the mechanism of disproportionation in alkyl radical reactions stated that "the disproportionation rate constant must be referred to the number of 'available' hydrogen atoms."[3] We shall refer to this as the "available hydrogen hypothesis" for disproportionation. It has been