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# Are Primary Quantum Yields of $NO_2$ Photolysis at $\lambda \leq 398$ nm Smaller than Unity?

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*Dedicated to Prof. Dr. Dr. h.c. mult. H. Gg. Wagner*
*on the occasion of his 70th birthday*

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***Photolysis / Atmospheric Chemistry / Elementary Gas Phase Reactions***

Primary quantum yields $\Phi$ of $NO_2$ photolysis at wavelengths $\lambda \leq 398$ nm and at bath gas pressures below 1 bar are analyzed. Stern-Volmer plots for collisional photolysis quenching, from experiments at pressures between 10 and 1000 bar, do not indicate a substantial reduction of the quantum yield below unity for pressures below 1 bar. The consequences of the recently discovered fluctuations of specific rate constants k(E) for $NO_2$ dissociation on collisional photolysis quenching are analyzed. These effects can lead to a small reduction of $\Phi$ at pressures below 1 bar which, however, is also smaller than the reduction reported in some experiments. Reanalysis of these experiments shows instead that, apart from experimental artifacts, the influence of the secondary reactions $O + NO_2 (+ M) \rightarrow NO_3 (+ M)$, $NO_3 + NO \rightarrow 2\,NO_2$, and $O + NO_2 \rightarrow O_2 + NO$ was underestimated. As a consequence, all experimental evidence so far is in favour of a low pressure primary quantum yield which is unity over the complete wavelength range 300–398 nm. This leads to a revised recommendation of quantum yields $\Phi$ for the range 300–430 nm at 298 K and 248 K. A revision of the limiting low pressure rate constant at 298 K of the reaction $O + NO_2 + N_2 \rightarrow NO_3 + N_2$ of $(1.6 \pm 0.2) \times 10^{-31}$ $[N_2]$ $cm^3$ $molecule^{-1}$ $s^{-1}$ is also recommended (to be employed together with $F_c = 0.6$ and a limiting high pressure value of $2.2 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$).

## 1. Introduction

Because of its crucial role in driving tropospheric photochemistry the photolysis

$$NO_2 + h\nu \rightarrow O + NO \tag{1}$$

has been studied over many decades. Absorption cross sections and quantum yields have been measured with increasing detail and precision (for a summary of references and results, see [1]). In spite of these efforts the reasons for a number of discrepancies have not completely been identified.

There are several measurements of the quantum yields at wavelengths $\lambda$ smaller than the photolysis threshold $\lambda_0 = 397.9534$ ($\pm 0.0008$) nm [2] which gave low pressure primary quantum yields below unity. So far no explanation of this observation has been presented. Photolysis quenching experiments at high bath gas pressures (up to 1000 bar) [3−5] and direct time-resolved photolysis experiments [6−8] (or the analysis of absorption line widths [9]) all led to specific rate constants k(E) for $NO_2$ dissociation in the range $10^{10}-10^{13}$ $s^{-1}$. From these results one would conclude that low pressure primary quantum yields should be equal to unity over the full range 300−398 nm. Values smaller than unity would indicate that nonreactive states of $NO_2$ exist above the dissociation energy. It is the aim of the present article to critically review the experimental evidence for quantum yields below unity and to estimate possible magnitudes of quantum yield reductions.

Primary quantum yields at $\lambda > \lambda_0$ fall off over several tens of nm. This effect in part is explained by the combined use of the photon energy and thermal rovibrational energy of the $NO_2$ molecules prior to excitation for breaking the O−NO bond [10]. In addition, collisional activation from initially nondissociative to dissociative states, during the anomalously long radiative lifetime of $NO_2$ [11], after excitation at $\lambda > 398$ nm can also lead to photodissociation [5, 12]. A semiquantitative master equation treatment of this mechanism has been presented in [5] and [12]. Recent progress in the calculation of the potential energy surface and of the specific rate constants k(E,J) for dissociation [13, 14] allows for a more quantitative modeling of this effect [15]: the centrifugal barriers $E_0(J)$ of the dissociation, which restrict the use of rotational energy for bond breaking, are better characterized; also collisional energy transfer now is better understood. Nevertheless, the uncertainties of quantum yield measurements at $\lambda < 398$ nm have also consequences for the experimental results at $\lambda > 398$ nm. It is aim of the present article to elucidate the origin of experimental uncertainties in order to arrive at a better quantum yield recommendation over the full wavelength range 300−430 nm.

## 2. Experimental low pressure quantum yields at $\lambda \leq 398$ nm

An excellent summary of earlier quantum yield measurements, identifying some artifacts in earlier work, has been presented together with extensive new data in [12, 16]. Table 1 shows the new results for $\Phi$, obtained at $NO_2$ pressures in the range 0.2 to 0.4 Torr and in the presence or absence of the buffer gas $N_2$. Although there is a trend of $\Phi$ to decrease when $\lambda$ increases

**Table 1.** Experimental primary quantum yields for $NO_2$ photolysis at 298 K.

| Wavelength ($\lambda$/nm) | Quantum yield | |
|---|---|---|
| | from [16][a] | from [12][b] |
| 334.1 | $0.99 \pm 0.05$ | |
| 364.9 | $1.01 \pm 0.07$ | |
| 378.6 | $0.98 \pm 0.04$ | |
| 383.8 | $0.97 \pm 0.06$ | |
| 394.0 | $0.95 \pm 0.07$ | $0.93 \pm 0.10$ (388−398 nm) |
| 396.8 | $0.89 \pm 0.05$ | |
| 404.3 | $0.36 \pm 0.04$ | 0.41 |

[a] At $NO_2$ pressures between 0.2 and 0.36 Torr; [b] at $N_2$ buffer gas pressures of 150 Torr.

towards $\lambda_0$, $\Phi$ is below unity outside of the specified uncertainty only at $\lambda = 396.8$ nm and at $\lambda > \lambda_0$. The most extensive earlier data from [17], obtained at low $NO_2$ pressures (between 0.5 and 4.5 Torr) and in the absence of a buffer gas, give $\Phi$ below unity also only at $\lambda \geq 390$ nm. However, the most recent and probably most careful measurements [12] between 388 and 398 nm led to $\Phi = 0.93 \pm 0.10$ at 298 K and $\Phi = 0.90$ at 248 K. In this case, buffer gas pressures of 150 Torr and 300 Torr of $N_2$ were employed. No wavelength dependence of $\Phi$ over the range 388−398 nm was noticed. The conclusion of these most recent experiments is, thus, that there exists a quantum yield reduction below unity at $\lambda < 398$ nm although this is not outside the experimental uncertainty. In the following we question this conclusion.

## 3. Collisional quenching of photolysis

One may ask whether buffer gas pressures of 150 Torr of $N_2$, such as applied in the experiments of [12], could have resulted in collisional quenching of the primary photolysis. The high pressure measurements of [3−5] led to linear Stern-Volmer representations of the primary quantum yields of the form

$$\Phi([N_2] \rightarrow 0)/\Phi([N_2]) = 1 + a(\lambda)[N_2] \qquad (2)$$

with $a(\lambda) = 35$, 45, 80, 110, and 210 $cm^3\ mol^{-1}$ for the wavelengths $\lambda =$ 385.5, 392, 394, 399, and 402 nm, respectively. At a buffer gas pressure of 150 Torr this corresponds to a quantum yield at 399 nm of $\Phi = 0.999$. This type of quenching, hence, cannot be the reason for a noticeable quantum yield reduction at $\lambda < \lambda_0$.

While Eq. (2) seems to rule out collisional quenching as a cause for marked primary quantum yield reductions at pressures below 1 bar, a new phenomenon has appeared on the scene which requires consideration. Quantum wavepacket calculations of $NO_2$ photodissociation [18] have indicated strong fluctuations of the specific rate constants $k(E,J=0)$. This is in agreement with experimentally observed linewidth fluctuations [9, 19] and also nonexponential decays of narrow-band excited $NO_2$ [18]. One has to investigate whether there is substantial collisional quenching of the most long-lived from the broad lifetime distribution of dissociative $NO_2$.

The distributions of fluctuating specific rate constants $k(E)$ were represented by a Porter-Thomas distribution of the form [20]

$$P(k) = \frac{N}{2\langle k\rangle}\left(\frac{Nk}{2\langle k\rangle}\right)^{N/2-1}\frac{\exp(-Nk/2\langle k\rangle)}{\Gamma(N/2)} \tag{3}$$

where $\langle k\rangle$ denotes the average of $k(E,J=0)$ and $k$ is the fluctuating specific rate constant. Fitting the experimental nonexponential decay of dissociating $NO_2$ molecules in [18] was achieved with parameters $N = 1.5 \pm 0.5$ of the distribution. The Stern-Volmer constants $a(\lambda)$ in Eq. (2) can be influenced by the rate constant distribution. As long as the Stern-Volmer plots are linear, the $a(\lambda)$ are related to $\langle k\rangle$ through

$$a(\lambda) \approx \gamma_c Z_{LJ}/k(E,J=0) = \gamma_c Z_{LJ}/\langle k\rangle \tag{4}$$

where $\gamma_c$ is a $\langle k\rangle$-dependent effective collision efficiency [21], $Z_{LJ}$ is the Lennard-Jones collision frequency, and the energy $E$ is related to the excitation wavelength $\lambda$. To a first approximation, we connect a fluctuation of specific rate constants with fluctuations of Stern-Volmer constants about the average $a(\lambda)$ such that

$$a/a(\lambda) = k(E,J=0)/k = \langle k\rangle/k\,. \tag{5}$$

On this level one may then estimate $\Phi$ from

$$\frac{\Phi([N_2])}{\Phi([N_2]\rightarrow 0)} \approx \int_0^\infty \frac{P(x)dx}{1 + a(\lambda)[N_2]/x}\,. \tag{6}$$

A more rigorous master equation treatment with Monte Carlo sampling from the distribution (3) appears premature at this stage. For several values of the parameter $N$ of the distribution, Table 2 compares quantum yields from Eq. (2) with values from Eq. (6); the product $a(\lambda)\,[N_2]$ from the linear Stern-Volmer plot (2) in this representation is used as wavelength-specific reduced concentration measure. One realizes that there is indeed an enhancement of the quantum yield reduction by collisional quenching. However, the effect is too small to account for quantum yield reductions to 0.93 at buffer gas pressures of 150 Torr. E.g. with $a(398\text{ nm}) \approx 100\text{ cm}^3\text{ mol}^{-1}$ and $N \approx 1.0$, $\Phi$ decreases from unity to about 0.99 at 150 Torr of $N_2$. The effect quickly becomes even less important at decreasing wavelengths. We conclude that lifetime fluctuations can have an influence on collisional

**Table 2.** Influence of lifetime fluctuations (Porter-Thomas distribution with parameters N in Eq. (3)) on quantum yields $\Phi$ ($\Phi_b$ from Eq. (6)) at different values of a($\lambda$) [$N_2$] in the Stern-Volmer plots ($\Phi_a$ from Eq. (2)).

| N | a($\lambda$) [$N_2$] | $\Phi_a$ | $\Phi_b$ |
|---|---|---|---|
| 1.5 | 0.0001 | 0.9999 | 0.9993 |
| | 0.001 | 0.9990 | 0.9936 |
| | 0.01 | 0.9901 | 0.9506 |
| | 0.1 | 0.9091 | 0.7710 |
| 1.0 | 0.0001 | 0.9999 | 0.9990 |
| | 0.001 | 0.9990 | 0.9905 |
| | 0.01 | 0.9901 | 0.9311 |
| | 0.1 | 0.9091 | 0.7278 |
| 0.5 | 0.0001 | 0.9999 | 0.9985 |
| | 0.001 | 0.9990 | 0.9857 |
| | 0.01 | 0.9901 | 0.9025 |
| | 0.1 | 0.9091 | 0.6720 |

quenching of photolysis but that the effect is too small to account for $\Phi$-values near 0.93 at buffer gas pressures near 150 Torr.

## 4. Reanalysis of secondary reactions

It is well known that secondary reactions of the photolysis (1) can influence the total quantum yields $\Phi_{tot}$ measured in photolysis experiments. In search of other possible reasons for quantum yield reductions, it appeared necessary to reinspect the influence of these reactions. At low buffer gas pressures, the reaction

$$O + NO_2 \rightarrow O_2 + NO \qquad (7)$$

dominates the sequence of possible secondary reacations and leads to $\Phi_{tot} = 2\,\Phi$ where $\Phi$, as before, denotes the primary quantum yield. With increasing pressures the sequence

$$O + NO_2 + M \rightarrow NO_3 + M \qquad (8)$$

$$NO + NO_3 \rightarrow 2\,NO_2 \qquad (9)$$

reduces $\Phi_{tot}$. Further reactions, forming $O_3$ and $N_2O_5$, with increasing pressure also enter $\Phi_{tot}$ [5]. However, for buffer gas pressures below 1 bar, only reactions (1), (7)−(9) matter, at quasistationary state leading to

$$\frac{\Phi}{\Phi_{tot}} = \frac{1}{2} + \frac{k_8([M])}{2\,k_7} \qquad (10)$$

where $k_8$([M]) denotes the pseudo-second order rate constant of reaction (8). Measurements of the pressure dependence of $\Phi_{tot}$ through Eq. (10) have provided an access to $k_8([M])$ as long as $k_7$ was measured independently. The data bases in use [1, 22] recommend values of $k_8([M])$ which were obtained in this way. There is only one direct measurement of $k_8([M])$ for 300 and 400 K at pressures above 1.5 bar from our laboratory [23], see below. Unfortunately, changes in $k_7$ have not consistently been translated into changes of $k_8([M])$. Furthermore, transfers of the ratio $k_8([M])/2\,k_7$ from one [M] to another require careful account of the falloff properties of the pressure-dependent rate coefficient $k_8([M])$. This is the issue of the following discussion. We argue that insufficient account of the term $k_8([M])/2\,k_7$ is responsible for the apparent quantum yield reduction below unity in the experiments from [12]. The influence of secondary reactions, of course, has been considered in the original evaluation of these experiments: using the data base from [22], a quantum yield reduction of 3% at 298 K and 150 Torr, and of 12% at 248 and 300 Torr was accounted for. In the following we show that these corrections were too small.

For 1 bar of $N_2$ and 298 K, the ratio $k_8([M])/k_7$ has been measured to be $0.33 \pm 0.08$ [24], $0.27 \pm 0.03$ [25], or $0.22 \pm 0.01$ [26]. The experiments of [25] were extended up to pressures of 1000 bar, giving $k_{8,\infty}/k_7 = 2.3 \pm 0.3$. Extrapolating down to 150 Torr of $N_2$ cannot simply be done by assuming that the low pressure limit is realized at 1 bar of $N_2$. Instead a full falloff curve has to be constructed in such a way that the experimental ratios of $k_8/k_7$ are reproduced at all pressures. We do this by the usual procedure [27] in expressing $k_8$ by

$$\frac{k_8}{k_{8,0}} \approx \left(\frac{1}{1 + k_{8,0}/k_{8,\infty}}\right) F_c^{\left[1 + \left(\log \frac{k_{8,0}}{k_{8,\infty}}\right)^2\right]^{-1}} \tag{11}$$

where we assume $F_c$ to be close to 0.6. In addition, we assume that $k_7$ is pressure independent. A more detailed theoretical prediction of $F_c$ is underway [23] but the used value of $F_c$ near 0.6 [28] well reproduces the experimental falloff curves from [23, 25]. This analysis leads to $k_8(150\ \mathrm{Torr})/k_{8,0} = 0.86$ and $k_8(1\ \mathrm{bar})/k_{8,0} = 0.70$ such that $k_8(150\ \mathrm{Torr})/k_7 = (k_8(1\ \mathrm{bar})/k_7) \times (0.86/0.70) \times (150/760)$. This gives a choice of $k_8(150\ \mathrm{Torr})/k_7$ ratios of $0.24 \times 0.33$, $0.24 \times 0.27$, and $0.24 \times 0.22$, depending on which of the *a priori* equivalent studies from [24−26] is preferred. The corresponding quantum yield reductions relative to the $P \rightarrow 0$ values are 7.9%, 6.5%, or 5.3%. Subtracting the 3% correction already accounted for in [12], instead of $\Phi = 0.93 \pm 0.1$ leads to $\Phi = 0.98$, 0.96, or 0.95. Allowing for another (1−2%) increase as a consequence of the lifetime fluctuations discussed in section 3, makes the measured quantum yield indistinguishable from unity.

It should be mentioned at this point that the given falloff analysis based on Eq. (11) with $F_c = 0.6$ also leads to a revised value of $k_{8,0}$. For the three measurements of [24−26] and a preferred value at 298 K of $k_7 = 9.7 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ [1] one derives $k_{8,0} = (1.85,\ 1.51,\ \text{or}\ 1.37) \times 10^{-31}$

**Table 3.** Recommended primary quantum yields for $NO_2$ photolysis at buffer gas pressures → 0 (measurements from [12], rescaled by forcing $\Phi$ ($\lambda < 398$ nm) to unity, see text).

| Wavelength ($\lambda$/nm) | Quantum yield $\Phi$ | |
|---|---|---|
| | at 298 K | at 248 K |
| 300−398 | 1.00 | 1.00 |
| 399 | 0.95 | 0.94 |
| 400 | 0.88 | 0.86 |
| 401 | 0.75 | 0.69 |
| 402 | 0.62 | 0.56 |
| 403 | 0.53 | 0.44 |
| 404 | 0.44 | 0.34 |
| 405 | 0.37 | 0.28 |
| 406 | 0.30 | 0.22 |
| 407 | 0.26 | 0.18 |
| 408 | 0.22 | 0.14 |
| 409 | 0.18 | 0.12 |
| 410 | 0.15 | 0.10 |
| 411 | 0.13 | 0.08 |
| 412 | 0.11 | 0.07 |
| 413 | 0.09 | 0.06 |
| 414 | 0.08 | 0.04 |
| 415 | 0.06 | 0.03 |

$[N_2]$ cm$^3$ molecule$^{-1}$ s$^{-1}$ instead of the recommended value of $9.0 \times 10^{-32}$ $[N_2]$ cm$^3$ molecule$^{-1}$ s$^{-1}$ from [1]. Averaging of these three values gives $k_{8,0} = (1.6 \times 10^{-31} \pm 0.2)$ $[N_2]$ cm$^3$ molecule$^{-1}$ s$^{-1}$. We note that this value is nicely consistent with the direct measurements from [23]. The low value from [1] is due to the preference of the data of [26], a choice of $F_c = 0.8$ instead of 0.6 as used here, and some internal inconsistency.

The effects discussed in sections 3 and 4 do not apply to the low pressure experiments from [16], for which a quantum yield reduction below unity at $\lambda < \lambda_0$ is outside the stated error limits only for the single wavelength of 396.8 nm where $\Phi = 0.89 \pm 0.05$ was found.

The discussed corrections from section 4 are wavelength independent. We, therefore, recommend to correct all quantum yield data from [12] upward by a factor of 1/0.93 at 298 K and 1/0.90 at 248 K. Table 3 gives the resulting new recommendation of low pressure quantum yields. The effects of quantum yield reductions by secondary reactions, in laboratory studies of $NO_2$ photolysis at 298 K, should be calculated with $k_7 = 9.7 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $k_{8,0} = (1.58 \pm 0.2) \times 10^{-31}$ $[N_2]$ cm$^3$ molecule$^{-1}$ s$^{-1}$, $k_{8,\infty} = 2.2 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ and $F_c = 0.6$.

## 5. Conclusions

In summarizing the preceding discussion we conclude that there is no experimental evidence for values below unity of the primary quantum yield of $NO_2$ photolysis at $\lambda < 398$ nm and at low gas pressures. This conclusion leads to a slight upward revision of recommended primary quantum yields for $NO_2$ photolysis in the wavelength range 300−430 nm.

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