

Direct NO₂ photolysis rate monitor

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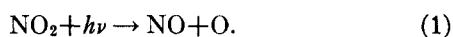
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An optically thin actinometer is described which measures the rate of photolysis of NO₂ in air. Operating details of the device are reported together with a test in downtown Detroit. The result was that the instrument was more accurate than some of the other test parameters in the range 0–0.5 min⁻¹. Applications to photochemical smog and stratospheric pollution problems are discussed.

INTRODUCTION

There is a general agreement^{1–3} that the chain-initiating reaction of photochemical smog is the photo-dissociation of NO₂ by ultraviolet sunlight, where



Kinetically, the reaction rate is expressed as

$$R = \int_{\lambda} \phi(\lambda) I(\lambda) k_a(\lambda) d\lambda,$$

where λ is the wavelength, $\phi(\lambda)$ is the quantum efficiency, $I(\lambda)$ is the intensity, and $k_a(\lambda)$ is the absorption coefficient of NO₂.⁴ We shall use $R_1 = k_1(\text{NO}_2)$, thus $k_1 = \phi I k_a$. This rate has proven difficult to measure in the ambient atmosphere.⁵

Reaction rates of photolytic dissociations are most often determined utilizing chemical actinometry to measure quantum yields.⁶ Classically, liquid actinometers such as potassium ferri-oxalate are employed, where the quantum efficiency is derived from the number of ferrous ions formed per quantum absorbed. While this approach is quite appropriate for laboratory experiments, examination of photodissociative processes occurring in smog chambers or the atmosphere necessitate the use of novel instrumentation, particularly to follow the rapid changes in solar intensity. Tuesday⁷ suggested the use of a pseudo-first-order rate constant, k_a , resulting from the photolysis of NO₂ in pure N₂, where $k_a = -d \ln(\text{NO}_2)/dt$. Subsequently, Holmes *et al.*⁸ have derived an expression for atmospheres not to exceed 10³ ppm oxygen. Nonetheless, this method does not measure continuously and is difficult to apply in the larger smog chambers, in view of the oxygen requirement.

Recently, Stedman and Niki⁹ reported a smog chamber technique that determines the NO₂ photolysis rate k_1 by following the buildup of photolysis products of NO₂ in air.

They found that in the first few seconds of photolysis of ppm NO₂ levels, the initial rate $-d(\text{NO}_2)/dt = d(\text{O}_3)/dt = d(\text{NO})/dt = k_1(\text{NO}_2)$. Rearrangement of their equation yields $k_1 = d(\text{NO})/dt(\text{NO}_2) = d(\text{O}_3)/dt(\text{NO}_2)$, and if time Δt and (NO_2) were held constant, then, $k_1 = C\Delta(\text{NO}) = C\Delta(\text{O}_3)$, where $C = 1/\Delta t(\text{NO}_2)$. Our instrument was based on this concept, but used a flow system for continuous measurement.

EXPERIMENTAL

To use this system as a continuous k_1 monitor, an ultraviolet transparent quartz tube was selected for a flow photolysis chamber. Such a tube permitted the establishment of regulated flows and provided for almost 4π steradian exposure to radiant flux. The photolysis chamber shown in Fig. 1 has an inner diameter of 2.2 cm and is 1 m long. It is open at one end to allow unrestricted exhaust of unused photolysis products at atmospheric pressure. The gas entrance end is closed except for 6.35 mm black tubing for a gas inlet. Upstream of the photolysis tube entrance is located a rotameter to monitor the total inlet gaseous flow rate F . A volume flow of 4.0 liters min⁻¹ of 1 ppm NO₂ provided a photolysis time Δt of 4 sec at a distance of 70.0

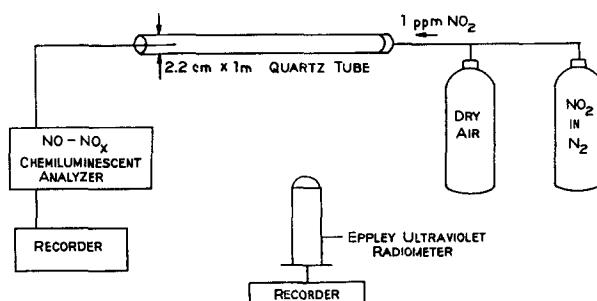


FIG. 1. A schematic diagram of the direct k_1 detector and the Eppley uv pyranometer with which it was compared.

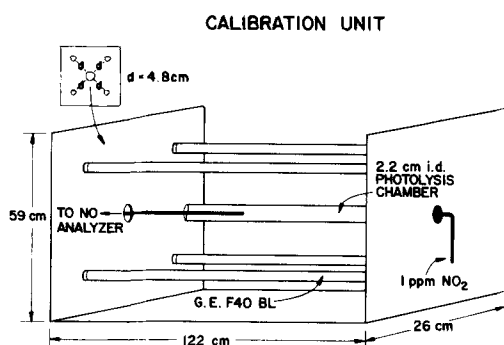


FIG. 2. Photolysis chamber for laboratory testing of the k_1 detector.

cm. The buildup of NO [$\Delta(\text{NO})$] and the initial (NO_2) was monitored with a Thermo-Electron model 12A chemiluminescent analyzer altered for direct capillary inlet to the vacuum system.

Equation (1) can be rewritten under flow conditions as

$$k_1 = \Delta(\text{NO}) / (\text{NO}_2) \times F / Ad. \quad (2)$$

The total flow, F , is measured with the previously calibrated flowmeter, and the cross-sectional area, A , and flow distance, d , are measured directly. A good feature of Eq. (2) is that the ratio of $\Delta\text{NO}/\text{NO}_2$ is measured. This ratio is independent of the absolute calibration accuracy of the NO detector, and only depends on the linearity, and the NO_2 converter efficiency,¹⁰ both readily checked.

Upstream from the inlet flowmeter is a Y-connection permitting the entrance of NO_2 in N_2 (Matheson Scientific nominally 100 ppm) and dry air, both from compressed gas tanks. Each cylinder was also monitored with rotameters to regulate flows, and thus the concentration of NO_2 at the photolysis chamber inlet.

For experimental purposes, it was necessary to design an illumination unit to test the k_1 detector concept. While several lamp arrangements and lamp-chamber distances were evaluated, the final model selected is depicted in Fig. 2. The lamps were General Electric F40BL black lights. Although a larger number of lamps could have provided a more intense radiant flux, the four-lamp design allowed a uniform flux and approximated average k_1 values for the ambient environment.

CALIBRATION

To calibrate the photolysis chamber, a series of experiments was performed to measure $\Delta(\text{NO})$ as a function of photolytic distance. The NO sampling probe was centered in the photolysis tube, with two windings of thin copper wire located near the tip of the glass capillary NO inlet. Similarly, another copper wire retainer was placed approximately 6 cm down the probe to aid in centering. Photolysis distances were measured using a one meter stick, and the glass capillary on the end of the NO inlet probe served to give a constant flow into the NO/ O_3 detector reaction chamber.

A test of this device was made by measuring (NO) and (O_3) as a function of distance along the flow tube [times up to 4 sec for various values of (NO_2)]. At 1 and 2 ppm NO_2 , linear and equal buildup of NO and O_3 were observed, as

TABLE I. Laboratory k_1 determinations four-lamp photolysis unit.

(NO_2) ₀ ppm	Flow- rate liters/min	$\Delta(\text{NO})$ ppm	$\Delta(\text{O}_3)$ ppm	Photolysis distance cm	k_1 min ⁻¹	(NO) ₀ ppb
1.0	4.0	0.014(4)		25	0.302	5
1.0	4.0		0.014(0)	25	0.295	
2.0	4.0	0.014(2)		50	0.298	8
2.0	4.0		0.013(8)	50	0.290	

predicted. At higher concentrations of NO_2 and for longer times, departures from linearity and NO exceeding O_3 were detected, as was predicted from the work of Stedman and Niki.¹¹ These experiments, which led to the choice of 4 sec and 1 ppm NO_2 , are fully documented by Jackson.¹² Table I shows one such consistency test using two concentrations of NO_2 and two photolysis distances. The (NO)₀ values represent an initial NO impurity in the NO_2 , which we had to measure and use as the baseline for our ΔNO measurements.

AMBIENT EXPERIMENT

This direct k_1 meter was utilized in two comparative experiments. One comparison was with k_1 calculated assuming an ambient photostationary state (PSS), where $k_1 = k_3(\text{NO})(\text{O}_3) / (\text{NO}_2)$. Stedman *et al.*¹³ report that direct $k_1 = 0.008(\pm 0.010) + 0.969(\pm 0.036)$ PSS k_1 . The values in parenthesis are two standard deviations, and the correlation coefficient is 0.993. This evidence, which was used to confirm the photostationary state assumption, also indicates the absolute accuracy of the k_1 detector.

The second comparison was with an Eppley uv pyranometer¹⁴ designed for overlap with the NO_2 absorption. Figure 3 shows a trace of Eppley uv and ΔNO as a function of time, with a slight displacement for clarity. The correlation which is evident in Fig. 3 was further confirmed by plotting all measured values of k_1 vs the Eppley reading in Fig. 4. Since the Eppley detector is looking upward (2π sr) and our direct k_1 monitor measures all illumination, then some discrepancy near the origin (at low sun angle) is expected, but the rest of the correlation is excellent. The value of the correlation line was $k_1 = 0.019 \pm 0.002$ E, where E is the Eppley reading in $\text{W} \cdot \text{m}^{-2}$. This correlation was obtained in Detroit for three weeks in August–September 1973.

To demonstrate that we can ignore any difficulties due to refraction and reflection in the cylindrical geometry, we rotated the tube into a range of orientations and observed

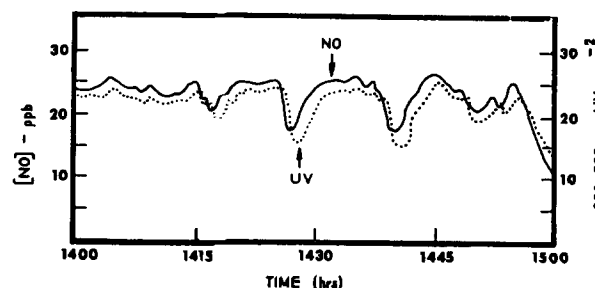


FIG. 3. The behavior of the k_1 detector and the Eppley uv meter on 26 August 1973, from 1400 to 1500 EDT.

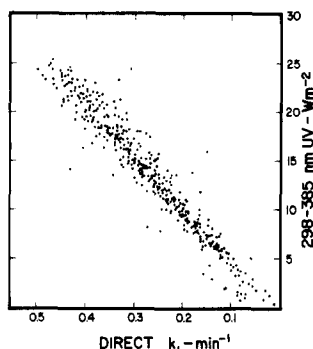


FIG. 4. Linear correlation between Eppley uv reading $W \cdot m^{-2}$ and direct k_1 (min^{-1}).

<5% change in signal, unless the stoppered end was pointed directly at the sun.

Further studies, which we would like to perform at other latitudes, might show some small differences in the Eppley correlation, but if this relationship is well maintained, it enables a simple photometer to give values of k_1 which can be used directly in photostationary state calculations, without the need for the increased expense and experimental difficulties of the direct k_1 monitor described herein.

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