Experimental determination of the photolysis constant of nitrogen dioxide for México City

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ABSTRACT

The photolytic rate constant of nitrogen dioxide is a key parameter in air quality models. We present the first actual measurements of this rate constant in México City. These were obtained with the use of an actinometer and the reactor, where a known concentration of NO_2 was photolysed for different experimental exposure times. Under the given experimental conditions, photolysis constants for NO_2 were determined during the day. This experiment is the first of its kind in Mexico.

INTRODUCTION

The experimental measurement of the NO_2 photolysis rate constant presents some difficulties. One has to take special care measuring the usually very low gas concentration, flow, reaction temperatures and other variables. Moreover, one should be able to minimize experimental errors arising from absorption, reflection and refraction at the walls of the tube, and shadowing by nearby instrumentation and structures.

A more practical way to continuously estimate NO_2 photolysis rate values is through establishing a semi-empirical correlation between discrete experimental values of these rates and solar actinic fluxes. (Jackson et al [1], Zafonte et al [5] and Madronich [2]).

Taking experimental values of the photolysis of NO_2 and solar fluxes from the literature, Madronich [5] proposed such a semi-empirical correlation. However, the data used by Madronich were obtained at 0.0, 0.3 1.8 and 3.0 km above sea level and latitudes above 33^0 North. Considering the need to have a similar correlation under México City conditions (2240 masl and 19^0 20' lat North) this work aimed to carry out experimental measurements of solar actinic fluxes and NO_2 photolysis rates.

PROCEDURE

A continuous flux actinometer is used in this work. In this, for different exposure times, a known concentration of NO_2 is photolysed. Steady state conditions are considered for the reaction mechanism of NO_2. (fig. 1)

R1	$NO_2 + h\nu$	$\rightarrow NO + O$
R2	$NO_2 + NO_3$	$\rightarrow N_2O_5$
R3	$NO_3 + h\nu$	$\rightarrow NO_2 + O$
R4	$NO_3 + h\nu$	$\rightarrow NO + O_2$
R5	$NO_3 + NO$	$\rightarrow 2NO_2$
R6	$O + NO_2$	$\rightarrow NO + O_2$
R7	$O + NO_3$	$\rightarrow NO_2 + O_2$
R8	$O + NO_2$	$\rightarrow NO_3$
R9	$O + NO$	$\rightarrow NO_2$
R10	N_2O_5	$\rightarrow NO_2 + NO_3$
R11		$\rightarrow$ wall

figure 1.- Reaction mechanism of NO_2

Thus,

$$\frac{d(NO_2)}{dt} = -(J + k')[NO_2]$$

where J is the photolysis constant and k' the wall constant. If the initial concentration of NO_2 is $[NO_2]_0$, (t=0)

$$\ln\left(\frac{NO_2}{[NO_2]_0}\right) = -kt$$

where $k=J+k'$. k' is estimated by measuring the concentration drop of NO_2 in the reactor which has been previously blocked from any incoming radiation.

EXPERIMENT

Figure 2 shows schematically the experimental configuration to measure the NO_2 photolysis rates and solar fluxes. A flux of NO_2 is pased through a regulator and a

flux meter (in particular, this flux is controled at 200 cm^3 /min). The NO_2 flux goes through a solenoid valve, where it can be diverted either to the quartz reactor or to the nitrogen chemiluminicent oxides analyser (Columbia Sc. In. Co., Model NA510-2). The reactor output is connected to the analyser in which concentrations of NO, NO_2 and NO_x are measured. Each one of these voltage outputs (one for each channel) is conected to a PC through a PCL812 data adquisitor (PC-LabDas [3]). A thermocouple J type, an Eppley radiometer, a pressure transductor and the PCL812 data adquisitor are connected to an amplifier PCL789 board. (PC-LabDas [3])

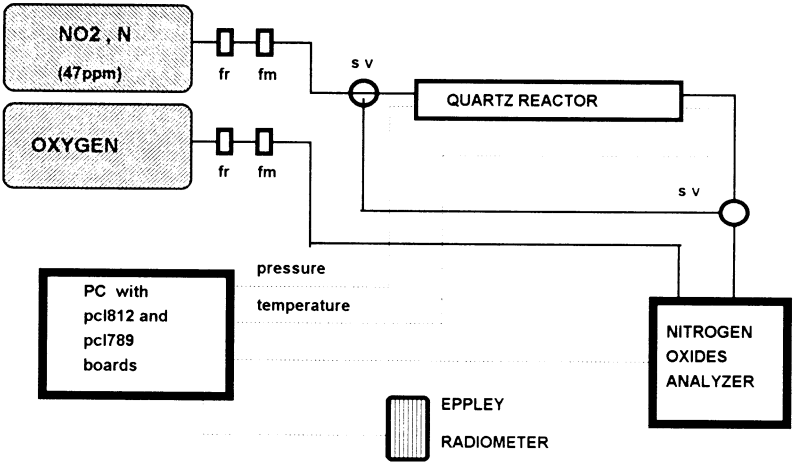

figure 2.- experimental diagram

The Eppley radiometer has a UV filter and a photocell placed behind a diffusing plate made of quartz. The espectral window is from 295 to 385nm. The NO_2, NO and NO_x data are measured by a nitrogen oxide analyser. This measures the chemiluminscent raction between NO and NO_2 . In order to have different exposure times.The length of the quartz reactor is changed during the experiments.

RESULTS AND CONCLUSIONS.

The experiment was carried out at the National University Campus (19^0 20', 2240 masl) the days 30 of November, 1,3 and 4 of December 1993. Measurements of temperature, pressure, UV radiation and NO, NO_2 and NO_x concetrations were obtained every minute. Four different reactor lengths (94, 74, 64 and 54cm) were used. Figure 3 shows the photolysis rate constants measured by the above procedure.

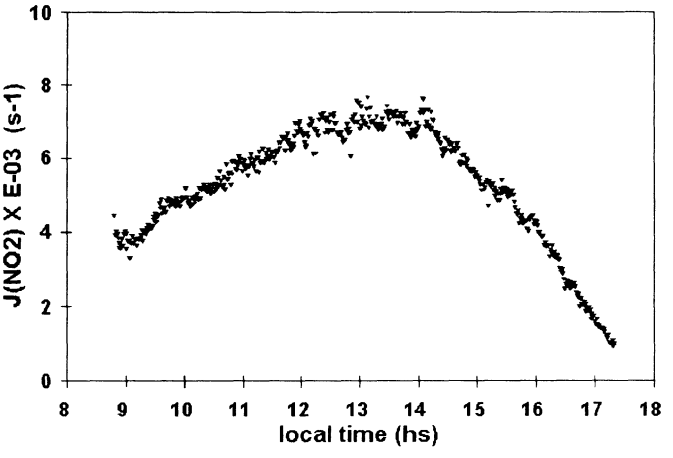

figure 3.- Photolyitic rate of NO_2

Figure 4 shows avereged UV fluxes. Figure 5 shows a plot of the NO_2 rates vs irradiances obtained in clear sky conditions. Figure 6 presents experimental NO_2 rates, the calculated ones (Ruiz-Suárez J.C. et al [4]), the estimated ones by equation 9 in Madronich [2] with UV irradiance experimental values and the calculated ones by eq. 12 in Madronich [2] considering 2240 masl.

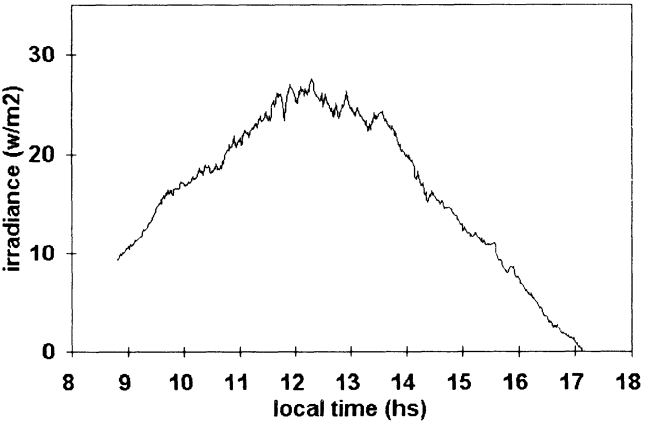

Figure 4.- Average UV irradiance for México City. (30Nov. 1,3 and 4 Dic., 1993)

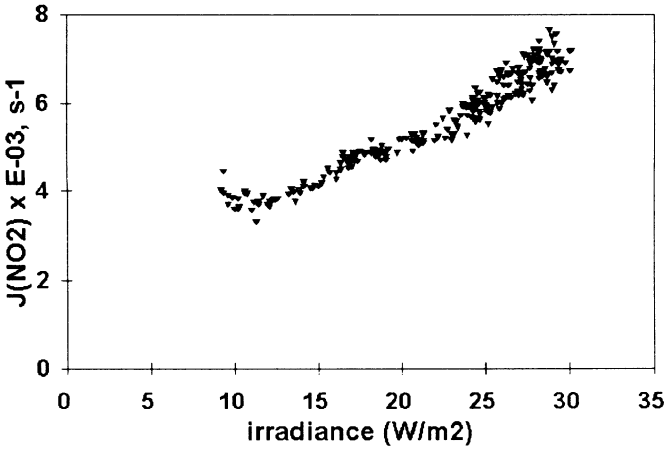

figure 5. Photolysis rate NO_2 vs UV rradiance obtained in clear sky conditions.

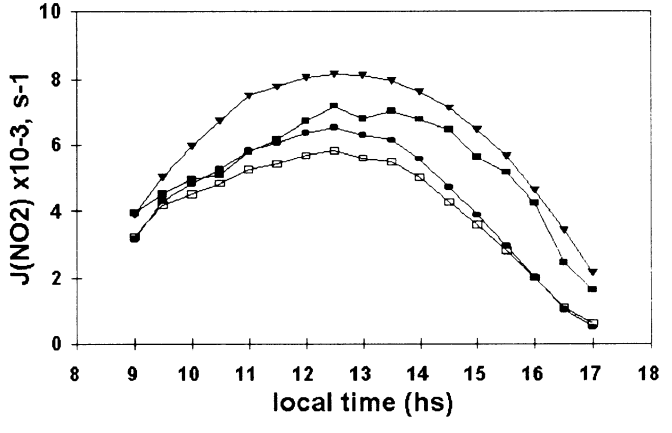

figure 6.- Comparision of photolytic rates of NO_2. Solid square are experimental values, solid triangles are theoretical values (Ruiz-Suárez et al [4]), solid circle and empty square are values obtained with eqs.9 and 12 in Madronich [2], respectively.

It is clear that the ready to use equation falls short of the experimental values of J, most likely because of local effects not present in the data set used to obtain the fitted constants. For this rason it seems reasonable to consider that the

semiempirical model may used provided *ad-hoc* local values of constants f and A_L (albedo) can be obtained.

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