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Photolysis of Nitrogen Dioxide to Produce Nitrogen Pentoxide

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Abstract

Nitrogen dioxide was photolyzed at room temperature in a long-path infrared cell. The concentrations of nitrogen dioxide and nitrogen pentoxide (N_2O_5) were followed as a function of time, and the molecular modulation spectrum of nitrogen dioxide was obtained in a steady-flow experiment. With one atmosphere of nitrogen, the observations were the rate constant ratios and standard deviations: $k_1[M]/k_2 = 0.18 \pm 0.01$, $k_3[M]/k_2 = 0.22 \pm 0.01$, $k_4/K = 0.71 \pm 0.02$ sec^{-1} where

1. $NO + O + M \rightarrow NO_2 + M$

2. $NO_2 + O \rightarrow NO + O_2$

3. $NO_2 + O + M \rightarrow NO_3 + M$

4. $NO_3 + NO \rightarrow 2NO_2$

$$K = ([N_2O_5]/[NO_2][NO_3])_{eq}$$

By using literature values for k_1 (6.9×10^{-32} cm^3 $molecule^{-1}$ sec^{-1}) and for K (1.24×10^{-11} cm^{-3}), the values of the elementary rate constants are: $k_2 = 9.2 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}, $k_3 = 8.2 \times 10^{-32}$ cm^6 $molecule^{-1}$ sec^{-1}, and $k_4 = 8.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}.

INTRODUCTION

The photolysis of nitrogen dioxide is a key reaction in photochemical air pollution[1], is important in stratospheric photochemistry[2], and is often used in the laboratory to measure light intensity between 300 and 400 nm. The reaction is complex, and there is disagreement in the literature as to the value of certain rate constants and rate-constant ratios. There is agreement in the literature[3,4,5] that the following mechanism describes the overall kinetics of the photolysis of small amounts of NO_2 in an inert carrier gas.

	Reaction	Rate
a.	$NO_2 + h\nu \rightarrow NO + O(^3P)$	$\alpha I [NO_2]$
1.	$NO + O + M \rightarrow NO_2 + M$	$k_1 [M][NO][O]$
2.	$NO_2 + O \rightarrow NO + O_2$	$k_2 [NO_2][O]$
3.	$NO_2 + O + M \rightarrow NO_3 + M$	$k_3 [M][NO_2][O]$
4.	$NO_3 + NO \rightarrow 2NO_2$	$k_4 [NO_3][NO]$
5.	$NO_3 + NO_2 + M \rightarrow N_2O_5 + M$	$k_{5M} [NO_2][NO_3]$
6.	$N_2O_5 + M \rightarrow NO_2 + NO_3 + M$	$k_{6M} [N_2O_5]$
7.	$O_2 + O + M \rightarrow O_3 + M$	$k_7 [M][O_2][O]$
8.	$NO + O_3 \rightarrow NO_2 + O_2$	$k_8 [NO][O_3]$

The purpose of this study was to examine this system with the molecular modulation technique[6], and in particular to focus on the rate constants for reactions 2, 3, and 4 at room temperature.

Quantities measured in this study were the decay of NO_2, the build-up and decay of N_2O_5, and the molecular modulation of NO_2 during intermittant illumination of a steady flow system. In terms of the mechanism these measurements give the following information: At low pressures (below 50 torr) the M-gas dependent reactions (1 and 3) become negligible compared to reaction 2, and the decay of nitrogen dioxide can be described by

$$\left(\frac{d \ln [NO_2]}{dt}\right)_{P \to 0} = -2 \alpha I \tag{1}$$

At one atmosphere total pressure and with small initial NO concentration, the disappearance of NO is given as a good approximation by

$$\ln \frac{[NO_2]}{[NO_2]_o} = \frac{-2\alpha It}{(1 + k_3[M]/k_2)} = -k_a t \tag{2}$$

where k_a is the empirical, first-order, decay constant. If the initial concentration of nitric oxide is close to zero, the initial rate of formation of dinitrogen pentoxide is

$$\left(\frac{d[N_2O_5]}{dt}\right)_{t \to 0} = \frac{\alpha I [NO_2]}{(1 + k_2/k_3[M])} \tag{3}$$

At an early stage of the reaction (t=t*) dinitrogen pentoxide goes through a maximum, at which point

$$\left(\frac{[N_2O_5]}{[NO_2]}\right)^* = \frac{\alpha I (K/k_4)}{(1 + k_2/k_3[M])} \left(\frac{[NO_2]}{[NO]}\right)^* \tag{4}$$

where $K = k_5/k_6$. The modulation amplitude of nitrogen dioxide in a steady flow system illuminated with square-wave photolyzing light of frequency f is

$$\frac{\Delta[NO_2]}{[NO_2]} = \frac{4\alpha I/\pi^2 f}{1 + \frac{k_1[NO]}{k_2[NO_2]} + \frac{k_3[M]}{k_2}} \tag{5}$$

It can be seen that Eq. 1 gives αI; with αI so determined, Eqs. 2 and 3 give two independent measures of the ratio k_2/k_3; the combination of Eqs. 1, 2, and 5 gives k_1/k_2.

Thus by solving the five experimental relationships simultaneously, it is possible to obtain values for αI, k_4/K, k_1/k_2, and k_3/k_2, with one equation redundant to use as a check. By taking the literature values for k_1 and for the equilibrium constant K, it is possible to obtain the elementary rate constants $\underline{k}_2$, $\underline{k}_3$, and $\underline{k}_4$.

EXPERIMENTAL

The instrument used in this work is a long path molecular modulation infrared spectrometer. A block diagram of the apparatus is shown in Figure 1. The reaction cell is a cylindrical quartz tube 91 cm long and 28.7 cm in diameter, with a volume of 67.0 liters. The cell is equipped with gold coated multiple reflection mirrows which give it a spectroscopic path length adjustable from 4 to 40 meters. The source of the IR radiation is a Nernest glower which is chopped at 400 cps by an American Time Products tuning fork. The monochromator is a McPherson

model 2051, one meter grating monochromator equiped with a
150 line per mm grating and order sorting filters. The IR
detector is a liquid helium cooled, copper doped germanium
photo conductor produced by the Santa Barbara Research Center.

The photolytic light for these experiments was supplied
by four, 32 inch G.E. 30 watt, F30T8/BL black lamps. The
photolytic photon flux in the cell is on the order of 10^{16}
photons/cm^2-sec. The photolysis lamp output for the cell is
monitored by a phototransistor, which can be used as a reference
to detect fluctuations in the lamp intensities. The photolysis
lamps are driven by a regulated power supply which can electronically
switch them on and off in response to a reference square wave from
a crystal oscillator.

The electronics for the instrument are designed to detect
the periodic concentration fluctuations in the absorbing gases
in the cell which are induced by the flashing of the photolysis
lamps. This is done by two sequential stages of demodulation.
The 400 cps AC signal from the detector carries the modulation
information on sidebands at 400±f cps, where f is the frequency
of the flashing lamps. The first demodulation is carried out by
a 400 cps lock-in amplifier which produces a DC signal directly
proportional to the spectroscopic light intensity. Riding on
this DC signal as a low frequency ripple is the modulation
information. This DC signal is split in two with one component
being recorded while the other is AC coupled, filtered, and
sent into the second stage of demodulation. The second stage
demodulator is a set of two lock-ins, operating at frequency f,

with one lock-in reference in phase with the photolysis lamps and one reference exactly 90° out of phase. The outputs of these two lock-ins represent the amplitude of the sine and cosine components of the first fundamental of the modulation signal. From these values the phase shift and amplitude of the modulation signal can be calculated. The output of all three lock-in amplifiers are recorded and time averaged in a signal averaging computer.

The carrier gases used in the experiments were high purity nitrogen and argon, both of which were passed through a Matheson water-and-particulate removal filter before use. The nitrogen dioxide used in the closed cell photolysis experiments was prepared by vacuum distillation from bulk liquid N_2O_4. The NO_2 used in the flow experiments was commercial mixed gas supplied by Matheson. The gas was analyzed by IR and UV spectroscopy in this laboratory and found to contain 970 ± 5 ppm NO_2 and 38 ± 4 ppm NO, with the remainder being N_2. The concentrations of all NO_x species involved in this work were determined spectroscopically from absorption coefficients measured in this laboratory.

RESULTS

A series of experiments was carried out in the closed cell with low total pressure, 19 to 56 torr. The decay of NO_2 was first-order throughout an experiment, and the results are listed in Table 1. When NO_2 is photolyzed in a closed cell at one atmosphere, the initial decay is first order, but deviations from first-order kinetics appear at later times, as illustrated

by Figure 2 (The concentration of NO_2 was followed by infrared absorption at 1600 cm^{-1}). Data for a series of experiments of this type are included in Table 1.

The build up and decay of N_2O_5 is illustrated by Figure 3 for conditions at one atmosphere total pressure (N_2) and 24°C. The concentration of N_2O_5 was followed by infrared absorption at 1238 cm^{-1}. The initial rate of formation of N_2O_5 is given in Table 2, and the concentrations of NO, NO_2, and N_2O_5 at the maximum value of N_2O_5 are given in Table 3. A plot of $([N_2O_5]/[NO_2])^*$ against $([NO_2]/[NO])^*$ is given as Figure 4, compare Eq. 4.

Along with these conventional measurements, a molecular-modulation study of NO_2 photolysis was carried out. The molecular-modulation method consists of monitoring the periodic concentration fluctuations induced in the reacting species by flashing the photolysis lamps on and off. In this work the NO_2 modulation was studied in a steady flow system with the photolysis lamps flashing at 1 cps. Under these conditions the NO_3 radicals and oxygen atoms will be at their steady state concentrations and N_2O_5 will be equilibrium.

The behavior of the concentration modulation of NO_2 can be described by a differential equation with the flashing lamps represented by the Fourier series for a square wave.

$$\frac{d[NO_2]}{dt} = \frac{F}{V}\left\{[NO_2]_{in} - [NO_2]_{out}\right\} - \left(\frac{k_2[NO_2]^2}{k_1[NO][M]+(k_2+k_3[M])[NO_2]}\right)$$

$$\left(\frac{2\alpha I}{\pi}\sum_{odd\ n}^{\infty}\frac{1}{n}\sin(n\omega t) + \alpha I)\right) \quad (6)$$

With: F = flow rate of chemicals

V = Volume of the reaction cell

$[NO_2]_{in}$ = the NO_2 concentration flowing into the cell

$[NO_2]_{out}$ = the NO_2 concentration flowing out of the cell

ω = 2π/T, where T is the period of the square wave

This equation neglects the ozone reactions, since the system contains no initial oxygen and the O_3 buildup will not be significant. Under these conditions the flow system has reached a steady state with respect to reactants and products, so the un-modulated or DC terms in Eq. 6 cancel leaving only the modulation or AC terms.

$$\frac{d[NO_2]_{AC}}{d\theta} = \frac{-\alpha I}{\pi^2 f} \frac{2k_2 [NO_2]^2 \sum\limits_{odd\ n}^{\infty} \frac{1}{n} \sin(n\theta)}{k_1 [NO][M] + (k_2+k_3)[M][NO_2]} \qquad (7)$$

where dθ = 2πfdt; θ = ωt; and f = flashing frequency.

Selecting the conditions so that the modulation will be less than one part per thousand leaves the reactant concentrations essentially constant, allowing Eq. 7 to be integrated in closed form to give:

$$[NO_2]_{AC} = \frac{\alpha I [NO_2]^2}{\pi^2 f} \frac{2k_2 \sum\limits_{odd\ n}^{\infty} n^{-2} \cos(n\theta)}{k_1 [NO][M] + (k_2+k_3)[M][NO_2]} \qquad (8)$$

By electronically filtering out all but the first Fourier component of the modulation signal, and taking the peak to peak amplitude gives the experimental relationship:

$$[NO_2]_{mod} = \frac{4\alpha I\, k_2 [NO_2]^2}{\pi^2 f(k_1 [NO][M] + (k_2 + k_3 [M])[NO_2])}$$ (9)

Comparison of Eqs. 8 and 6 shows the NO_2 modulation waveform to be triangular, phase shifted 90° from the exciting light. The amplitude of this waveform and its phase shift from the exciting light can be determined experimentally and related to Eq. 9.

A summary of the steady state concentrations with the phase shift and amplitude measurements are recorded in Table 4. The photolytic light intensity for the modulation experiments was found to be 11.2% greater than in the initial slope experiments, when measured by the phototransistor mounted in the cell, and the values of αI have been normalized by this factor.

DISCUSSION

The observed rate constant ratios are assembled in Table 5. The two independent values of k_3/k_2 agree within 10 per cent; the value based on Eq. 2 was more precise and is preferred. The three observed ratios, k_1/k_2, k_3/k_2, and k_4/K, are compared with values reported in the literature in Table 6.

This study gives only rate ratios. To evaluate absolute values of rate constants, either k_1, k_2, or k_3 must be taken from the literature. Of the three, the most extensive and most precise data are those for k_1. Literature values are summarized in Table 7, and the value 6.9×10^{-32} cm^3 molecule^{-1} sec^{-1} was taken for N_2 as foreign gas at room temperature. The observed quantity k_4/K is reduced to k_4 by the literature value of K.

With these values of K and k_1, the elementary rate constants k_2, k_3, and k_4 are evaluated and listed in Table 8 with the other 8 elementary rate constants in this system.

With these 8 elementary reactions, a computer program was written that integrated the simultaneous rate equations to give NO_2 and N_2O_5 as a function of time. In Figures 2 and 3 the circles represent observations and the smooth curves are those calculated from the elementary rate constants in Table 8. There is good agreement between the calculated and observed curves over the full course of observations.

ACKNOWLEDGEMENT

Table 1.   Initial rate of decay of NO_2 as a function of pressure

$[NO_2]$ molecules cm^{-3}	Total pressure torr	Relative light int.	k_a sec^{-1} Eq. 2
8.6×10^{14}	19.5	1.00	1.47×10^{-2}
8.8×10^{14}	19.5		1.44×10^{-2}
4.8×10^{14}	22		1.50×10^{-2}
8.8×10^{14}	27		1.52×10^{-2}
12×10^{14}	56		1.52×10^{-2}
6.7×10^{14}	756	1.00	1.23×10^{-2}
9.6×10^{14}	756		1.20×10^{-2}
10.5×10^{14}	756		1.25×10^{-2}
11.6×10^{14}	756		1.22×10^{-2}
2.1×10^{14}	756	0.56	0.69×10^{-2}
2.4×10^{14}	756		0.71×10^{-2}
3.1×10^{14}	756		0.68×10^{-2}
19.7×10^{14}	756		0.68×10^{-2}

Temperature 24°C

NO_2 followed by infrared absorption at 1600 cm^{-1}

Table 2. Initial rate of formation of N_2O_5

$[NO_2]$ molecules cm^{-3}	$\dfrac{\lim(d[N_2O_5]/dt)_{t \to 0}}{[NO_2]}$ sec^{-1}
1.91×10^{15}	0.73×10^{-3}
2.5×10^{15}	0.69×10^{-3}
2.6×10^{15}	0.64×10^{-3}
2.8×10^{15}	0.63×10^{-3}
3.3×10^{15}	0.70×10^{-3}
3.3×10^{15}	0.79×10^{-3}

Table 3. Conditions at maximum concentration of N_2O_5

Initial concentrations		Concentrations at N_2O_5 maximum		
molecules cm^{-3}		molecules cm^{-3}		Ratio
$[NO_2]$ $\times 10^{-15}$	$[NO]$ $\times 10^{-14}$	$[N_2O_5]$ $\times 10^{-13}$	$[NO_2]$ $\times 10^{-15}$	$\dfrac{[NO][N_2O_5]}{[NO_2]^2}\times 10^3$ $[NO]$
3.28	0.0	2.1	2.82	1.14
3.26	0.0	2.0	2.79	1.13
2.50	0.0	1.43	2.13	1.06
2.84	0.0	1.66	2.43	1.08
1.85	8.1	0.89	1.59	1.11
1.61	10.2	0.65	1.37	1.11
2.56	16.5	0.84	2.21	0.91
2.56	25.2	0.68	2.19	0.87
2.26	25.8	0.80	1.95	1.16
2.36	40.8	0.57	2.00	1.05

Table 4. Data for NO_2 modulation at one atmosphere total pressure, 24°C

Carrier gas	Steady state concentration		k_a sec^{-1} $\times 10^3$	phase shift degrees	$\Delta [NO_2]$ mod. $\times 10^{-11}$	$\dfrac{k_1 [M]}{k_2}$
	$[NO_2]$ $\times 10^{-14}$	$[NO]$ $\times 10^{-15}$				
N_2	1.02	0.74	8.3	93.6	1.43	0.163
N_2	1.19	1.22	8.3	89	1.31	0.179
N_2	0.68	1.49	8.3	70	1.40	0.189
N_2	1.13	2.04	8.3	82	0.83	0.185
N_2	1.87	2.12	8.3	80	1.62	0.190
N_2	1.68	1.60	7.2	94	1.68	0.178
Ar	1.55	1.38	8.3	88.2	1.78	0.190
Ar*	2.12	1.30	4.6	87.8	1.65	0.206
Ar	1.34	1.34	8.3	91.8	1.41	0.198

Table 5. Observed rate constant and rate constant ratios

Rate constant function	Observed value	Based on equation	Source of data	Condition
αI	7.45×10^{-3} sec^{-1}	(1)	Table 1	
k_a	1.22×10^{-2} sec^{-1}	(2)	Table 1	1 atm N_2
$k_3[M]/k_2$	0.22	(2)	Table 1	1 atm N_2
k_3/k_2	8.9×10^{-21}	(2)		$N_2 = M$
$k_3[M]/k_2$	0.20	(3)	Table 2	1 atm N_2
k_3/k_2	8.1×10^{-21}	(3)		$N_2 = M$
k_4/K	0.71 sec^{-1}	(4)	Table 3, Fig. 4	
$k_1[M]/k_2$	0.18	(5)	Table 4	1 atm N_2
k_1/k_2	7.3×10^{-21}	(5)		$N_2 = M$
$k_1[M]/k_2$	0.20	(5)	Table 4	1 atm Ar
k_1/k_2	8.1×10^{-21}	(5)		$Ar = M$

Table 6. Comparison of the results of this work with the
          literature values

$k_1[M]/k_2$	$k_3[M]/k_2$	k_4/K (sec^{-1})	T°K	Ref.
0.18±.01	0.221±.005	0.71±.02	296	This work
0.18±.004	0.33±.08		296	7
0.10±.05	0.27±.03		295	5
0.36	1.9		300	4
		0.60±.06	296	8

Total Pressure = 1 Atmosphere

M Gas = Nitrogen

Table 7. Observed values of k_1

k_1 (cm^6/molecule^{-1} sec^{-1})	M gas	T	Ref
$7.0\pm.08\times10^{-32}$	O_2, N_2, Ar	296	9
$7.6\pm.05\times10^{-32}$	Ar, O_2	300	10
$6.4\pm0.8\times10^{-32}$	O_2	297	11
$7.3\pm0.9\times10^{-32}$	N_2	297	11
$5.1\pm0.2\times10^{-32}$	O_2, He, Ar	293	12
5.3×10^{-32}	Ar	298	13
6.1×10^{-32}	N_2	298	14
$10.0\pm0.14\times10^{-32}$	N_2	296	15

Ave. value = 6.9×10^{-32} cm^6/molecule-sec

Table 8. Elementary rate constants for nitrogen dioxide
          photolysis, 297°K, 1 atm N_2

Constant	Value	Source	Ref.
k_1	6.9×10^{-32} cm^6 sec^{-1}	Literature	[9-15]
k_2	9.2×10^{-12} cm^3 sec^{-1}	k_1, k_1/k_2	Table 5
k_3	8.2×10^{-32} cm^6 sec^{-1}	k_2, k_3/k_2	Table 5
K	1.24×10^{-11} cm^{-3}	Literature	[16]
k_4	8.7×10^{-12} cm^3 sec^{-1}	K, k_4/K	Table 5
k_{6M}	0.104 sec^{-1}	Literature	[17]
k_{5M}	1.29×10^{-12} cm^3 sec^{-1}	K, k_{6M}	
k_7	6.24×10^{-34} cm^{-6} sec^{-1}	Literature	[18]
k_8	2.1×10^{-14} cm^3 sec^{-1}	Literature	[19]

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21

TITLES TO FIGURES

Fig. 1. Schematic diagram of experimental apparatus.

Fig. 2. NO_2 decay; comparison of experimental points and
calculated curve based on rate constants in Table 8.
Initial concentrations: $[NO_2] = 4.2 \times 10^{15}$, $[NO] =$
2.05×10^{14}.

Fig. 3. N_2O_5 decay as observed by infrared absorption at 1237
cm^{-1}; comparison of experimental points and calculated
curve based on rate constants in Table 8. Initial
concentrations: $NO_2 = 2.8 \times 10^{15}$ molecules cm^{-3}, $[NO] = 0$.

Fig. 4. Concentration ratios where nitrogen pentoxide is a
maximum, Equation 4.

Fig. 1

XBL 728-6830

-22-
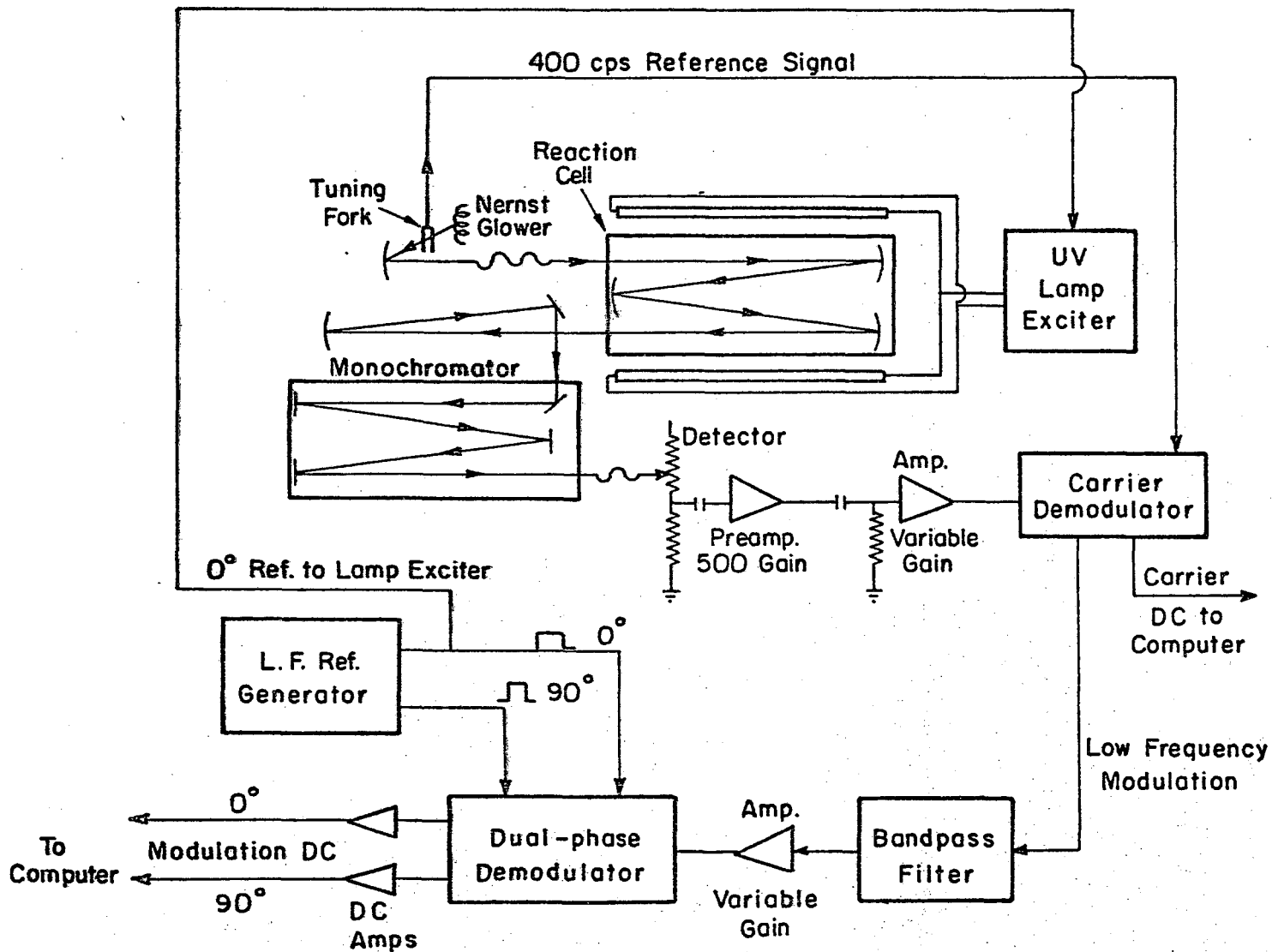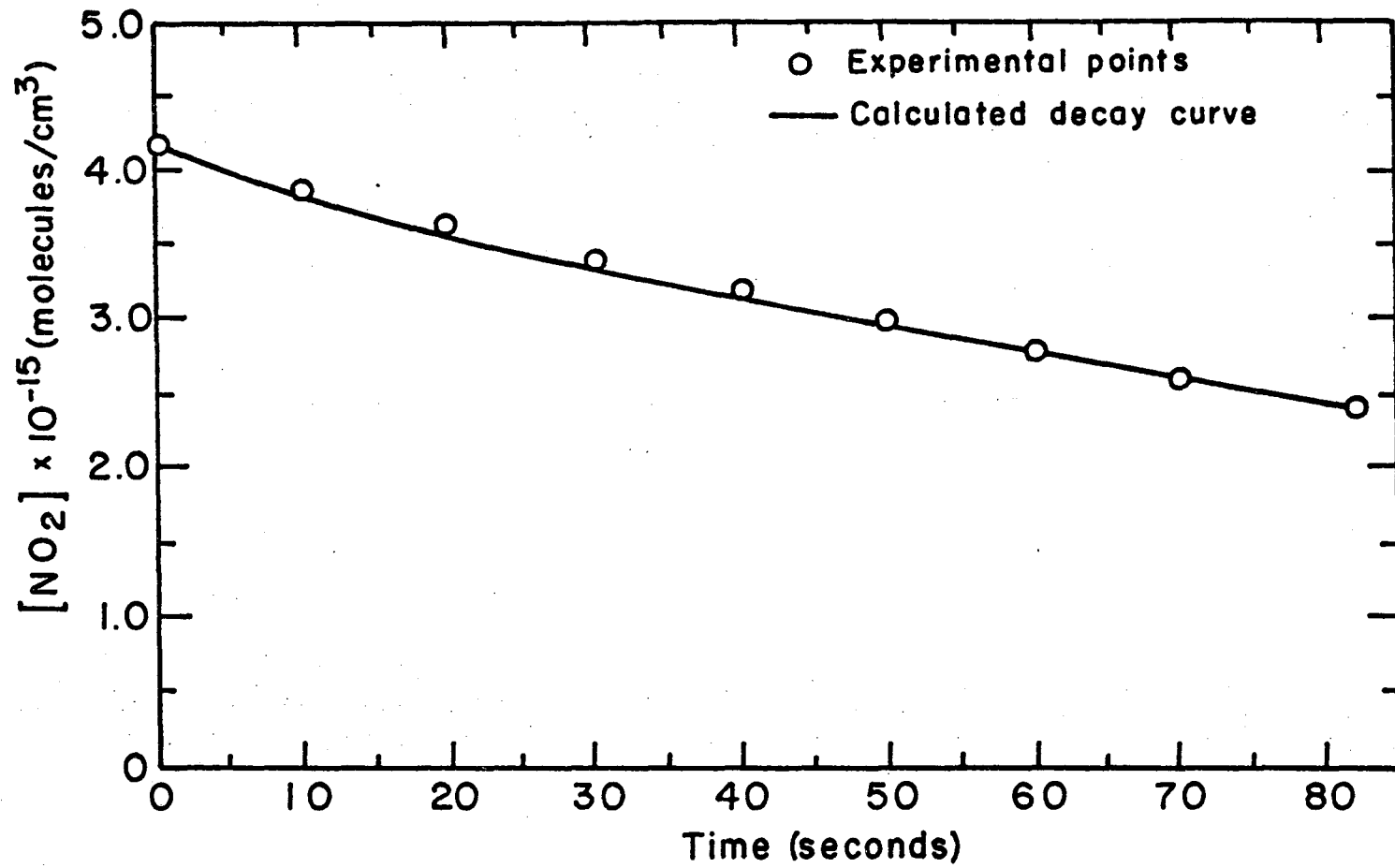
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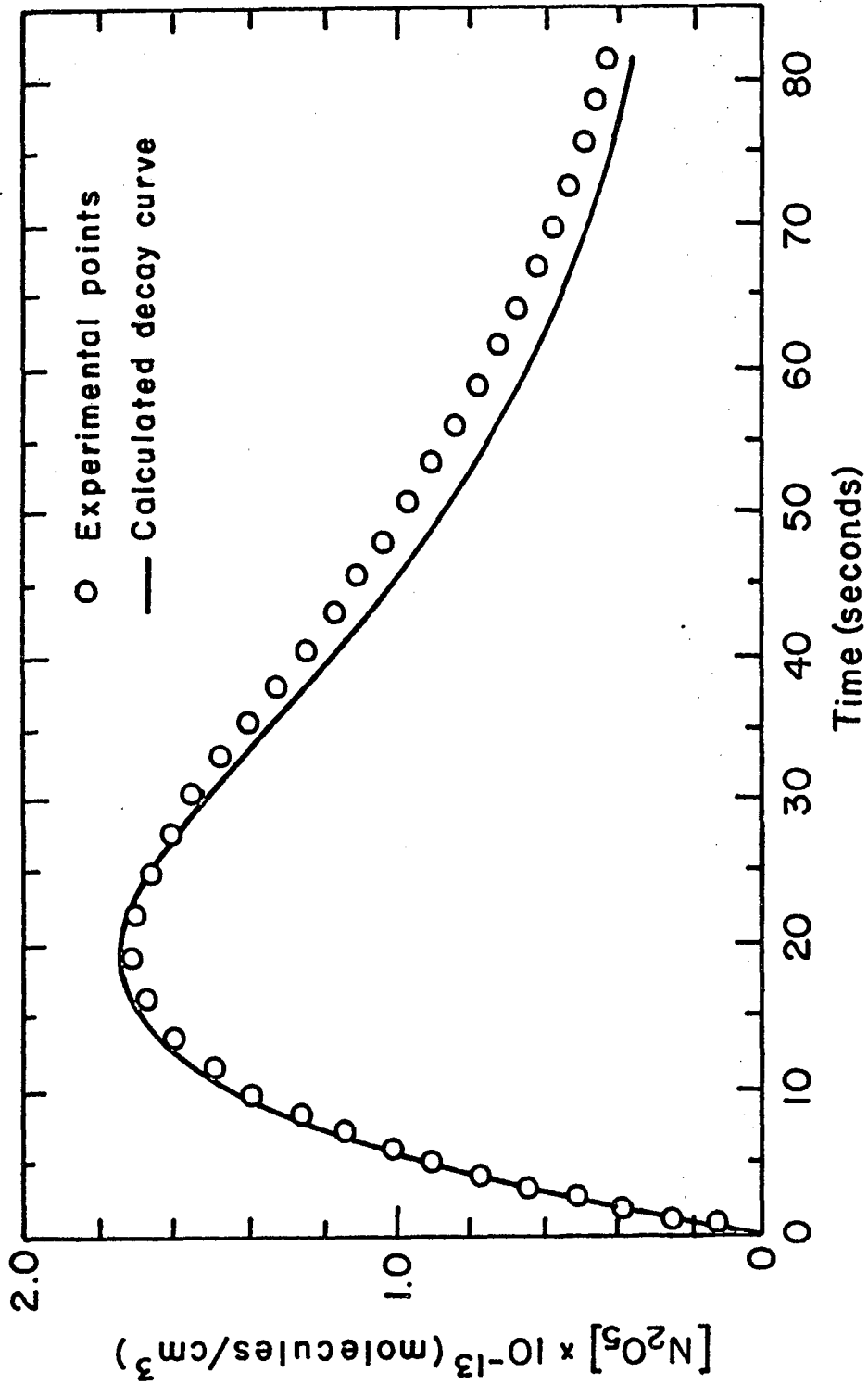
XBL728-6843

XBL728-6845

Fig. 3
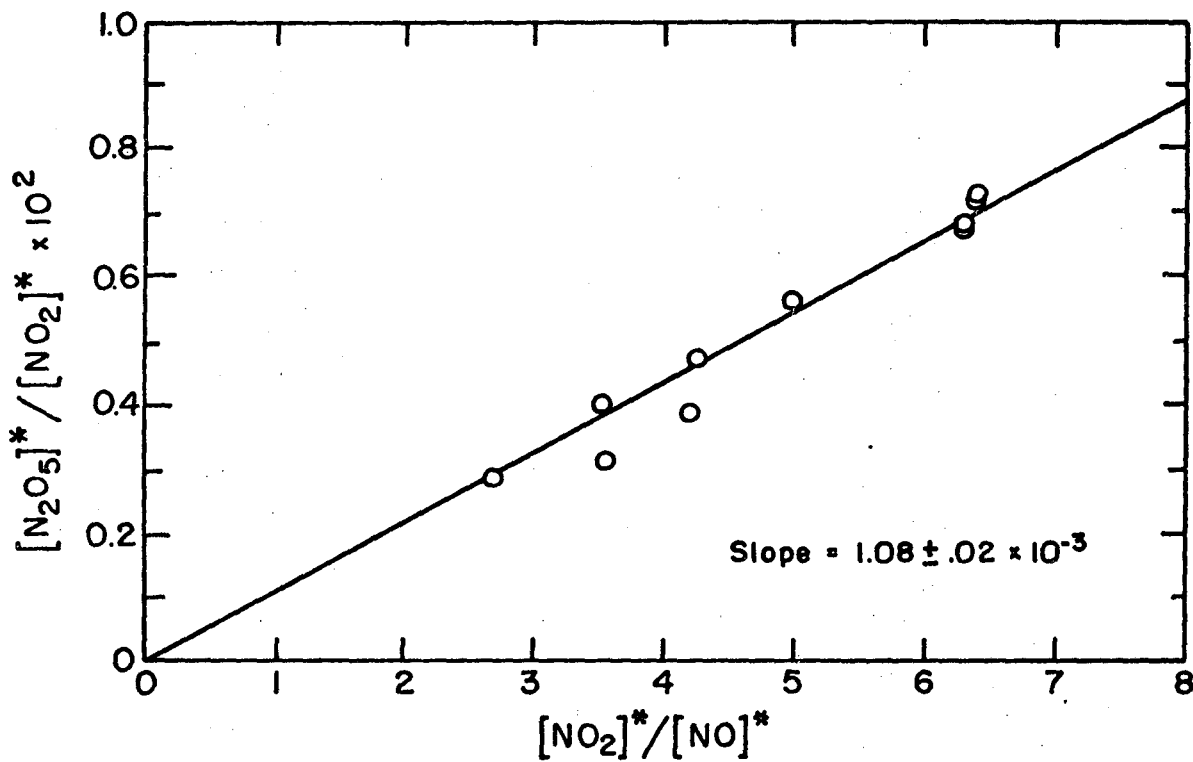
The * indicates the concentration at the time of the N_2O_5 concentration maximum, t^*

XBL 728-6842

Fig. 4