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CALCULATION OF SELECTED PHOTOLYTIC RATE CONSTANTS OVER A DIURNAL RANGE:
A Computer Algorithm

Environmental Sciences Research Laboratory
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CALCULATION OF SELECTED PHOTOLYTIC RATE CONSTANTS OVER A DIURNAL RANGE

A Computer Algorithm

by

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ABSTRACT

An increasing number of mathematical models are being developed which theoretically simulate the chemical reactions that comprise the urban smog formation mechanism. These models have necessitated the development of a technique for the accurate and efficient calculation of photolytic rate constants for certain smog-related chemical species. A computer program has been created and is described herein which employs the theoretical formulation of the photolytic rate constant to calculate these rate constants for specific chemical species over a diurnal time period in clear-sky conditions. A user of the program must specify the date, time and location for which the rate constants are desired. With this information and specific data on zenith angles, solar irradiance, and species characteristics of absorption cross-sections and primary quantum yields, which are provided in the program package, the computer program generates a diurnal range of photolytic rate constants for each species. The species included are NO_2, O_3, HONO, $HONO_2$, H_2CO, CH_3CHO, and H_2O_2. Provision is made for the addition or deletion of species as the user desires. The appendices to this report contain program and data listings as well as a User's Guide to program operation.

The program-generated photolytic rate constants for NO_2 are compared to direct measurements of this quantity as taken at Research Triangle Park, N.C. during April 1975. The two methods are generally in close agreement after the theoretically computed rate constants are scaled by a simplistic method for the compensation of solar radiation attention by clouds.

This report covers a period from 7/75 to 3/76 and work was completed as of 3/76.

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SECTION 1

INTRODUCTION

The driving force behind the chemical kinetic mechanism which is responsible for smog formation in urban atmospheres is solar radiation. The rate at which the mechanism proceeds is, in large part, controlled by the intensity of this radiation. Key chemical species such as nitrogen dioxide, nitrous acid, and certain oxygenated hydrocarbons absorb light in specific wavelength bands and are consequently photodissociated. These reactive product species subsequently participate in chain reactions comprising the hydrocarbon-NO_x oxidation process.

Controlled chamber studies have simulated the processes by which photochemical smog is created.[1,2] They have documented the direct proportionality between light intensity, rates of hydrocarbon-NO photo-oxidation, and ozone production. Further, an increasingly better understanding of the complex chemical kinetic mechanism of smog formation has led to the development of models which theoretically simulate the reactions in the mechanism.[3] Several of these chemical kinetic models have been incorporated into larger regional photochemical air quality simulation models (PAQSM). The accuracy in the specification of the photolytic rate constants within the chemical model is paramount in producing a credible simulation of regional air quality in a PAQSM. A typical simulation in such a model might extend from sunrise until late afternoon, during which time the light intensity of solar radiation varies through a diurnal cycle of values. The predicted levels of ozone from the model run have been shown to be highly sensitive to variations in solar light intensity.[4,5] The photolytic rate constants which are input to the model must accurately reflect the diurnal changes in this radiation intensity.

Increasing sophistication in the developing chemical kinetic models for smog formation is allowing more photolytic species to be included. There exists a need, therefore, for the generation of photolytic rate constants for these species over a diurnal range in an accurate and efficient manner so as to produce compatible input to the present and future generations of chemical kinetic models and PAQSM's. A computer program has been developed which helps to fill this need. Presented with information concerning latitude, longitude, and date for a specific location, the program will generate photolytic rate constants for various species over a preselected diurnal time range at a specified time interval ($1 \text{ min} \leq \Delta t \leq 60 \text{ min}$). Currently, the photolytic species included in the program are NO_2, O_3 (three reactions), HONO, $HONO_2$, H_2CO (two reactions), CH_3CHO (two reactions), and H_2O_2.

SECTION II

THEORETICAL FORMULATION

The rate expression for a primary photochemical reaction, such as the photolysis of NO_2,

$$NO_2 + h\nu \rightarrow NO + O \qquad (1)$$

is described by

$$\frac{-d(NO_2)}{dt} = k_{NO_2} \cdot (NO_2) \qquad (2)$$

where k_{NO_2} is the photolytic rate constant for the reaction. The rate of photolysis of NO_2 is dependent upon the efficiency with which the species absorbs light. This efficiency varies over the wavelength range of absorption. For NO_2, the absorptive range of wavelengths extends from 290 nm to approximately 440 nm. It is also possible, therefore, to describe the rate expression for NO_2 photolysis by

$$\frac{-d(NO_2)}{dt} = \sum_{\lambda = 290nm}^{440nm} I_a(\lambda) \cdot \phi(\lambda) \qquad (3)$$

where $I_a(\lambda)$ is the rate of photon absorption per unit volume of air containing NO_2 at a specific wavelength, λ, and $\phi(\lambda)$ is the primary quantum yield, or the number of molecules of NO_2 dissociated per photon absorbed at a specific wavelength λ. The primary quantum yield, $\phi(\lambda)$, by definition, cannot exceed unity. From equations (2) and (3) it follows that

$$k_{NO_2} \cdot (NO_2) = \sum_{\lambda = 290nm}^{440nm} I_a(\lambda) \cdot \phi(\lambda) \qquad (4)$$

or,

$$k_{NO_2} = \frac{1}{(NO_2)} \sum_{\lambda = 290nm}^{440nm} I_a(\lambda) \cdot \phi(\lambda) \qquad (5)$$

The rate of photon absorption, $I_a(\lambda)$, is estimated using the weak absorption form of the Beer-Lambert Law, an appropriate approximation for the low concentration of ambient pollutants considered in this application[8]. As a result, $I_a(\lambda)$, is proportional to the concentration of the species, its absorption cross-section, $\sigma(\lambda)$, and the actinic irradiance, $J(\lambda)$, or the radiation intensity integrated over all angles as seen by a sample of absorbing species; or

$$I_a(\lambda) = (NO_2) \cdot \sigma(\lambda) \cdot J(\lambda) \qquad (6)$$

The photolytic rate constant for the reaction described in (1) now takes the form

$$k_{NO_2} = \sum_{\lambda = 290nm}^{440nm} J(\lambda) \cdot \sigma(\lambda) \cdot \phi(\lambda) \qquad (7)$$

where the variables on the right-hand side of the expression are either measured or calculated. For clear sky conditions and an assumed surface-albedo function, the actinic irradiance is functionally dependent upon the solar zenith angle, ϕ, a spatially and temporally varying quantity, and altitude h. Thus for a specific location and altitude, $J(\lambda,\theta,h)$, and hence, k_1, will strictly be a function of time.

More generally, the rate constant for the photodissociation of species i in the lower atmosphere may be expressed as

$$k^i(\theta,h) = \sum_{\lambda = 290nm}^{800nm} J(\lambda,\theta,h) \cdot \sigma^i(\lambda) \cdot \phi^i(\lambda) \qquad (8)$$

where $k^i(\theta,h) \equiv$ photolytic rate constant (sec^{-1}) for species i at solar zenith angle θ and altitude h,

$J(\lambda,\theta,h) \equiv$ radiation intensity (photons cm^{-2} sec^{-1}) averaged over wavelength interval $\Delta\lambda$ centered about λ at solar zenith angle θ and altitude h,

$\sigma^i(\lambda) \equiv$ absorption cross sections (cm^2) for species i averaged over wavelength interval $\Delta\lambda$ centered about λ,

$$\sigma^i(\lambda) = (n\ell)^{-1} \log_e (I_0/I).$$

where n is the concentration of species i (molecules cm^{-3}), ℓ is the path length (cm), and I_0 and I are incident and transmitted radiation respectively,

and $\phi^i(\lambda) \equiv$ primary quantum yield of species i averaged over wavelength interval $\Delta\lambda$ centered about λ.

The current version of the computer algorithm does not permit a variation in altitude in $J(\lambda,\theta)$. Rate constants are generated, therefore, for only one altitude at a time, typically the level being some representative average for approximately the first several tens of meters or so above ground. Typical variations of k_{NO_2} with altitude have recently been discussed by Peterson[7].

$J(\lambda,\theta)$ values used by the program were selected as follows. The original working version of the algorithm utilized $J(\lambda,\theta)$ data from Leighton[8]. His values are averaged over 10-nm wavelength intervals and are representative of average solar irradiance at or near the earth's surface in a cloud-free atmosphere. In his treatment of the calculation of $J(\lambda,\theta)$, Leighton invoked several simplifying assumptions in his approach to Rayleigh scattering, aerosol scattering, and absorption of light within the atmosphere. These values may be contrasted with the actinic irradiance data calculated recently by Peterson[9] using a sophisticated radiative transfer model (RTM) developed by Dave[10]. This model also treats the vertical variation in $J(\lambda,\theta,h)$. Several of the differences between Leighton's approach and that of Peterson are illuminating. First, Leighton assumed the surface of the earth to be nonreflective, whereas Peterson used a surface albedo of 5 to 15% as a function of wavelength. This difference manifests itself in the fact that the newest values of the actinic flux are 5 to 11% higher in the ultraviolet wavelengths and up to 30% higher at the longest wavelengths than those of Leighton. Second, evidence suggests that the solar constant data available to Leighton were about 9% too high. This effect has been corrected in the latest model. Third, the climatological data available to

Leighton on the total amount of atmospheric ozone, based on Dobson spectrophotometer measurements, has been amended so that contemporary values are about 35% higher than the earlier values. The higher climatological values of total ozone as currently used resulted in significantly lower actinic fluxes at wavelengths below about 325nm. Lastly, Leighton assumed that half the scattered radiation from atmospheric aerosols was directed backward, whereas the RTM handles the large majority of this radiation as directed forward. Leighton's aerosols therefore caused more depletion of the actinic flux than did the aerosols used by Peterson[9]. The present version of the rate constant computer program incorporates values of $J(\lambda,\theta)$ calculated by Peterson for his lowest model level, which is representative of the atmosphere from the surface to around 50m. These actinic fluxes, based on typical atmospheric aerosol and ozone profiles, were calculated to represent general conditions in the continental U.S. The data have been averaged over 10-nm wavelength intervals from 290 to 700nm. It has been necessary to extrapolate Peterson's $J(\lambda,\theta)$ data for wavelengths from 700 to 800nm to satisfy at least one species which absorbs light at these longer wavelengths. To calculate photolytic rate constants for an altitude other than the surface level, the $J(\lambda,\theta,h_j)$ values may be obtained for the particular level j from the RTM and be used in place of the $J(\lambda,\theta,h_{sfc})$ values in the program, leaving all other parameters the same.

In order to gain some insight into the effect of the newly calculated actinic fluxes on photolytic rate processes, a comparison is presented in Table 1 of the calculated photolytic rate constants at selected zenith angles using the actinic flux data reported by Peterson[9] and those reported by Leighton[8]. The wavelength ranges of radiative absorption for each of the listed processes are described in the next section.

TABLE 1. A COMPARISON OF CALCULATED PHOTOLYTIC RATE CONSTANTS FOR REACTION PROCESSES USING ACTINIC FLUXES REPORTED BY PETERSON AND (LEIGHTON[8])*

PROCESS	k, sec^{-1}			
θ =	0°	20°	40°	60°
$NO_2 + h\nu \rightarrow O(^3P) + NO$	9.64×10^{-3} (1.00×10^{-2})	9.33×10^{-3} (9.67×10^{-3})	8.25×10^{-3} (8.46×10^{-3})	5.94×10^{-3} (5.93×10^{-3})
$O_3 + h\nu \rightarrow O(^3P) + O_2$	5.51×10^{-4} (5.16×10^{-4})	5.36×10^{-4} (5.01×10^{-4})	4.82×10^{-4} (4.51×10^{-4})	3.79×10^{-4} (3.44×10^{-4})
$\rightarrow O(^1D) + O_2$	7.02×10^{-5} (1.33×10^{-4})	6.22×10^{-5} (1.17×10^{-4})	4.04×10^{-5} (7.37×10^{-5})	1.42×10^{-5} (1.99×10^{-5})
$\rightarrow O_2(^1\Delta) + O$	1.21×10^{-4} (1.93×10^{-4})	1.10×10^{-4} (1.74×10^{-4})	7.92×10^{-5} (1.21×10^{-4})	3.66×10^{-5} (4.86×10^{-5})
$HONO + h\nu \rightarrow HO + NO$	5.41×10^{-4} (5.83×10^{-4})	5.22×10^{-4} (5.61×10^{-4})	4.56×10^{-4} (4.86×10^{-4})	3.22×10^{-4} (3.34×10^{-4})
$HONO_2 + h\nu \rightarrow HO + NO_2$	5.28×10^{-7} (9.58×10^{-7})	4.71×10^{-7} (8.52×10^{-7})	3.10×10^{-7} (5.48×10^{-7})	1.11×10^{-7} (1.51×10^{-7})
$H_2CO + h\nu \rightarrow HCO + H$	3.57×10^{-5} (4.51×10^{-5})	3.35×10^{-5} (4.23×10^{-5})	2.68×10^{-5} (3.37×10^{-5})	1.53×10^{-5} (1.86×10^{-5})
$\rightarrow CO + H_2$	9.33×10^{-5} (1.08×10^{-4})	8.88×10^{-5} (1.03×10^{-4})	7.43×10^{-5} (8.61×10^{-5})	4.74×10^{-5} (5.39×10^{-5})
$CH_3CHO + h\nu \rightarrow CH_3 + HCO$	7.08×10^{-6} (1.01×10^{-5})	6.55×10^{-6} (9.31×10^{-6})	4.90×10^{-6} (6.91×10^{-6})	2.39×10^{-6} (3.10×10^{-6})
$\rightarrow CH_4 + CO$	1.50×10^{-7} (3.17×10^{-7})	1.31×10^{-7} (2.75×10^{-7})	8.12×10^{-8} (1.63×10^{-7})	2.63×10^{-8} (4.17×10^{-8})
$H_2O_2 + h\nu \rightarrow 2HO$	2.72×10^{-5} (3.24×10^{-5})	2.58×10^{-5} (3.07×10^{-5})	2.14×10^{-5} (2.52×10^{-5})	1.34×10^{-5} (1.53×10^{-5})

*Calculated photolytic rate constants using Leighton's actinic fluxes from Demerjian and Schere[6].

SECTION III

PHOTOLYTIC SPECIES DATA

The method of computing photolytic rate constants for various chemical species, as given by equation (8), demands certain pertinent information concerning each species: the wavelength range over which it absorbs light must be known, as well as the values of the absorption cross-section throughout this range, and also the primary quantum yields for the same wavelength intervals as the absorption cross-sections. For the purposes of the computer program, the data were averaged over 10-nm wavelength intervals in all cases, centered at $\lambda = 290nm, 300nm, \ldots, 800nm$.

The specific photolytic reactions for which rate constants are automatically generated and the sources of the required species information are listed below.

$$NO_2 + h\nu\ (\lambda \leq 440nm) \rightarrow NO + O(^3P) \qquad (9)$$

The values of absorption cross-section for NO_2 were taken from a National Bureau of Standards review by Hampson[11], while the corresponding primary quantum yield data are those given in another NBS review by Hampson and Garvin[12].

$$HONO + h\nu\ (300nm < \lambda < 400nm) \rightarrow HO + NO \qquad (10)$$

$$HONO_2 + h\nu(\lambda \leq 300nm) \rightarrow HO + NO_2 \qquad (11)$$

Absorption cross-sections for both HONO and $HONO_2$ are those reported in Johnston and Graham[13]. The primary quantum yield values for $HONO_2$ were taken from the same source, while those for HONO were assumed equal to unity over the full absorption range shown in reaction (10).

$$O_3 + h\nu\ (310nm < \lambda < 350nm;\ 450nm < \lambda < 750nm) \rightarrow O(^3P) + O_2 \qquad (12)$$

$$O_3 + h\nu\ (\lambda \leq 310nm) \rightarrow O(^1D) + O_2 \quad (13)$$

$$O_3 + h\nu\ (\lambda \leq 350nm) \rightarrow O_2(^1\Delta) + O \quad (14)$$

Ozone participates in three distinct photolytic reactions: (12), (13), and (14). The absorption cross-sections are identical for corresponding wavelength intervals in the above reactions. They were calculated from spectra reported by Griggs[14]. The primary quantum yields, as taken from Hampson[15], differ, however, according to the reaction for which they are applicable.

$$H_2CO + h\nu\ (\lambda < 370nm) \rightarrow H + HCO \quad (15)$$

$$H_2CO + h\nu\ (\lambda < 370nm) \rightarrow H_2 + CO \quad (16)$$

Formaldehyde undergoes two photolytic processes, one of which contains free radical products (15) while the other results in molecular products (16). The absorption cross-sections and primary quantum yield data for both reactions are those reported in Calvert et al.[16]

$$H_2O_2 + h\nu\ (\lambda < 370nm) \rightarrow 2HO \quad (17)$$

Absorption cross-sections for hydrogen peroxide are those reported in Leighton[8](p. 86), and primary quantum yields were assumed equal to unity over the entire absorption range.

$$CH_3CHO + h\nu\ (\lambda < 350nm) \rightarrow CH_3 + HCO \quad (18)$$

$$CH_3CHO + h\nu\ (\lambda < 320nm) \rightarrow CH_4 + CO \quad (19)$$

The absorption cross-sections for acetaldehyde were taken from Calvert and Pitts[17]. The primary quantum yield data were based on the studies of Blacet, Loeffer, and Heldman[18, 19]. The limited quantum yield information suggests that the photolysis rate constants reported here represent a lower limit estimation. An upper limit for the acetaldehyde photolysis rate constant may be estimated by assuming a primary quantum yield of one over the absorptive region of interest.

SECTION IV

DESCRIPTION OF COMPUTER PROGRAM

The task of calculating the photolytic rate constants is performed by a user-oriented computer program which operates with a given complement of seven chemical species. There is adequate flexibility in the program to delete existing species or add new ones. The FORTRAN code is composed of a main program segment, six subroutines, and one function. A listing is provided in Appendix A, a sample data set in Appendix B, and the User's Guide in Appendix C of this report.

Figure 1 portrays a flow chart of the logic invoked by the program. Several blocks of input data are required to initiate program operation. First, the user must specify the location (by latitude, longitude, and time zone), the date (month, day, and year), and time (both time range and increment) for which the photolytic rate constants are to be generated. The full range of wavelength values over which there are corresponding inputs of actinic flux, $J(\lambda,\theta)$, is specified next as well as the wavelength increment used to average the quantities $J(\lambda,\theta)$, $\sigma(\lambda)$, and $\phi(\lambda)$. The current version of the program employs a wavelength range of 290nm to 800nm with an increment of 10nm. Zenith angle values, θ, which have corresponding inputs of $J(\lambda,\theta)$ are next specified. Presently ten values of θ from 0° to 86° are used. Figure 2 shows the matrix form of $J(\lambda,\theta)$ data which must be input at this point. Actual values used from Peterson[9] are included in the sample data set presented in Appendix B. Upon completion of these data inputs, the program has been initialized.

As the flow of logic in Figure 1 shows, program control now passes into the loop which is responsible for generating the photolytic rate constants over the specified diurnal time range for each chemical species. For each species being photolyzed, the wavelength range of absorption, absorption cross-sections, $\sigma(\lambda)$, and primary quantum yields, $\phi(\lambda)$, must be specified. The program subroutines are now called upon to perform their individual tasks in the

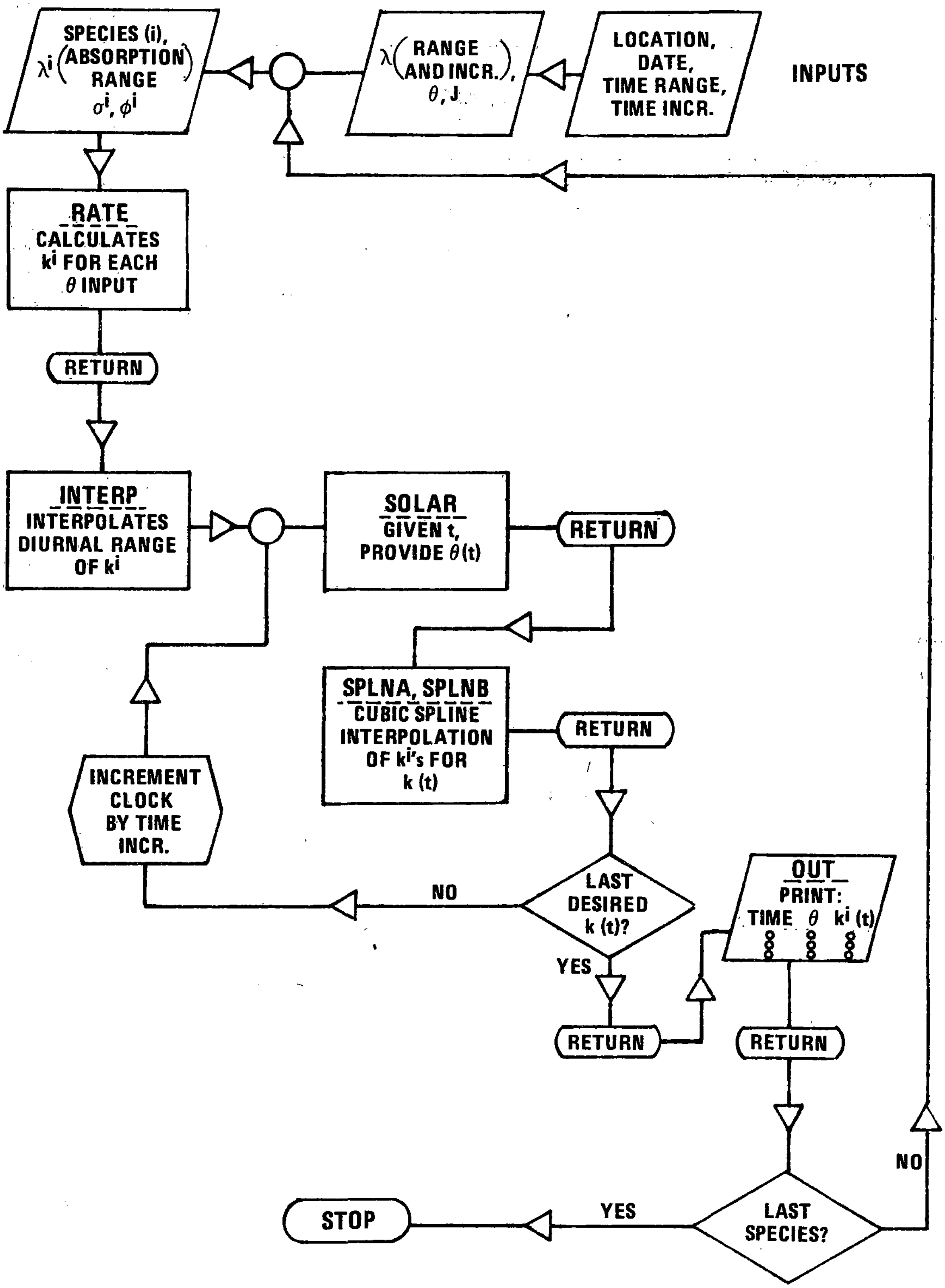

Figure 1. Flow diagram of logic controlling computer program to calculate photolytic rate constants.

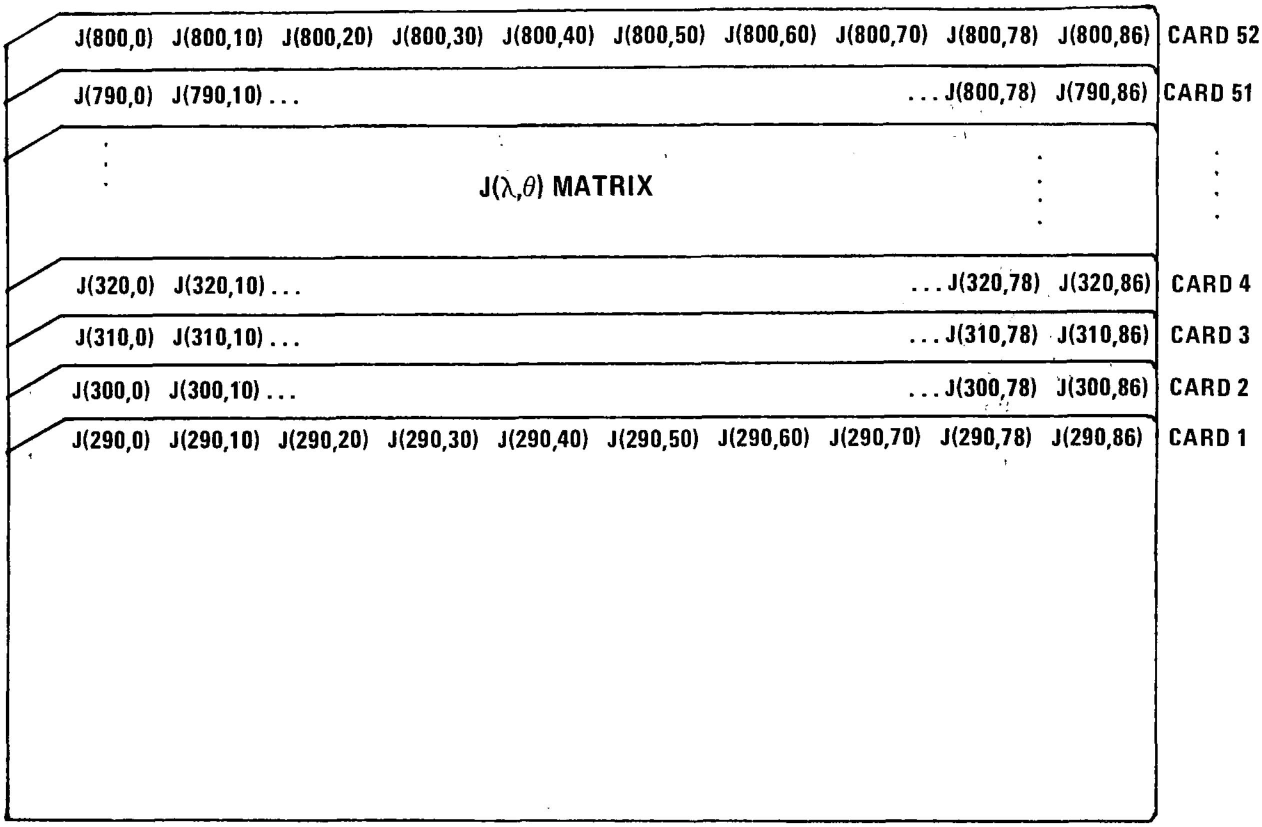

Figure 2. Card deck set-up for data input of $J(\lambda, \Theta)$ matrix invoked by photolytic rate constant program.

remaining steps of the rate constant calculations. They are briefly described here.

A. Subroutine RATE

This routine calculates rate constants for a given species, i, at each of the zenith angles specified in the inputs. The general form for the theoretical formulation of the photolytic rate constant is that given in equation (8). This is the form utilized by RATE, with the range of the summation corresponding to the limits of the absorptive wavelength range.

B. Subroutine INTERP

The logic control for the inner loop seen in the flow chart in Figure 1 is presented in this subprogram. Provided with a tabulation of θ and $k^i(\theta)$ at the input values of zenith angle as calculated by

RATE, the inner loop generates interpolated $k^i(\theta)$'s corresponding to θ values over the specified diurnal time range of interest. INTERP calls upon several of the remaining subroutines to do this.

C. Subroutine SOLAR

This subroutine was written by Busse[20], based on a paper by Woolf[21]. Given the information on location, date, and time, SOLAR returns a value of solar elevation angle, from which the zenith angle, θ, is readily found. The basic working equation used by this subprogram for the solar elevation angle is

$$\sin \alpha = \cos \phi \sin D + \cos \phi \cos D \cos h \quad (20)$$

where α = solar elevation angle, ϕ = latitude,

D = declination angle of the sun, and h = solar hour angle, a measure of the longitudinal distance to the sun from the point for which the calculation is being made.

D. Subroutines SPLNA, SPLNB

In these subroutines a set of n points is exactly fit with an interpolating function made up of n-1 cubics. Given three consecutive points, the cubic between x_{i-1} and x_i must agree with the cubic between points x_i and x_{i+1} at the point x_i in both the first and second derivatives. The n points used by the cubic interpolation scheme consist of those $(\theta, k^i(\theta))$ pairs computed in RATE.

E. Subroutine OUT

Finally, the results of the photolytic rate constant calculations are printed in tabular form in the temporal sequence as specified by the diurnal time range and increment. An example of the printed output for a run of the program for Los Angeles, California on June 21, 1975 follows in the next section.

Upon completion of the print cycle for species i, program control again returns to the point at which species parameters of λ range, $\sigma(\lambda)$, and $\phi(\lambda)$ must be provided. The rate constant calculations are then performed again for the new species.

SECTION V

SAMPLE OUTPUT AND INTERPRETATION

The following table contains a complete listing of program results for 11 species photolyzed in Los Angeles, California on June 21, 1975.

TABLE 2. PROGRAM RESULTS FOR L.A., JUNE 21, 1975

PHOTOLYTIC RATE CONSTANTS, K, FOR VARIOUS SPECIES AS A FUNCTION OF TIME AND ZENITH ANGLE

LOCATION:	LOS ANGELES, CALIF.			
LATITUDE:	34.058			
LONGITUDE:	118.250			
DATE:	6	21	1975	
TIME:	400	TO	2100	LOCAL STANDARD TIME

(continued)

TABLE 2. (continued) SPECIES: NO2

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

Z (ZENITH ANGLE) (DEGREES)	K (RATE CONSTANT) (/SEC)
.00	.9640-02
10.00	.9560-02
20.00	.9325-02
30.00	.8905-02
40.00	.8250-02
50.00	.7278-02
60.00	.5937-02
70.00	.3849-02
78.00	.1894-02
86.00	.4073-03

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.950	.0000
445	90.259	.0000
500	87.513	.1506-03
515	84.717	.6249-03
530	81.876	.1123-02
545	78.994	.1682-02
600	76.075	.2336-02
615	73.124	.3066-02
630	70.144	.3813-02
645	67.137	.4522-02
700	64.108	.5173-02
715	61.058	.5754-02
730	57.992	.6258-02
745	54.911	.6691-02
800	51.819	.7071-02
815	48.719	.7418-02
830	45.614	.7741-02
845	42.508	.8035-02
900	39.405	.8298-02
915	36.311	.8526-02
930	33.232	.8724-02
945	30.178	.8895-02
1000	27.159	.9044-02
1015	24.195	.9172-02
1030	21.312	.9280-02
1045	18.550	.9370-02
1100	15.977	.9441-02
1115	13.704	.9494-02
1130	11.905	.9529-02
1145	10.823	.9548-02
1200	10.678	.9550-02
1215	11.507	.9536-02
1230	13.124	.9506-02
1245	15.282	.9458-02
1300	17.782	.9393-02
1315	20.497	.9308-02
1330	23.350	.9206-02
1345	26.294	.9083-02
1400	29.299	.8941-02
1415	32.345	.8776-02
1430	35.418	.8586-02
1445	38.508	.8367-02
1500	41.609	.8115-02
1515	44.715	.7829-02
1530	47.820	.7514-02
1545	50.922	.7175-02
1600	54.017	.6806-02
1615	57.101	.6390-02
1630	60.172	.5908-02
1645	63.226	.5348-02
1700	66.262	.4717-02
1715	69.275	.4024-02
1730	72.263	.3284-02
1745	75.223	.2542-02
1800	78.152	.1861-02
1815	81.044	.1277-02
1830	83.898	.7653-03
1845	86.707	.2876-03
1900	89.469	.0000
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.348	.0000
2030	104.690	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued)

SPECIES: HONO

INITIAL DATA POINTS USED IN SUBSLOPE CALCULATIONS:

(ZENITH ANGLE) (DEGREES)	k (RATE CONSTANT) (/SEC)
.00	.5413-03
10.00	.5364-03
20.00	.5219-03
30.00	.4960-03
40.00	.4560-03
50.00	.3973-03
60.00	.3218-03
70.00	.1993-03
78.00	.9550-04
86.00	.2127-04

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.950	.0000
445	90.259	.0000
500	87.513	.8629-05
515	84.717	.3199-04
530	81.876	.5665-04
545	78.994	.8472-04
600	76.075	.1182-03
615	73.124	.1566-03
630	70.144	.1973-03
645	67.137	.2379-03
700	64.198	.2764-03
715	61.058	.3110-03
730	57.992	.3403-03
745	54.911	.3646-03
800	51.819	.3856-03
815	48.719	.4034-03
830	45.614	.4246-03
845	42.508	.4427-03
900	39.405	.4589-03
915	36.311	.4729-03
930	33.232	.4850-03
945	30.173	.4954-03
1000	27.159	.5045-03
1015	24.195	.5124-03
1030	21.312	.5191-03
1045	18.550	.5247-03
1100	15.977	.5291-03
1115	13.704	.5324-03
1130	11.905	.5345-03
1145	10.823	.5357-03
1200	10.673	.5358-03
1215	11.507	.5350-03
1230	13.124	.5331-03
1245	15.282	.5302-03
1300	17.782	.5261-03
1315	20.497	.5209-03
1330	23.350	.5145-03
1345	26.294	.5070-03
1400	29.299	.4982-03
1415	32.345	.4882-03
1430	35.418	.4766-03
1445	38.508	.4632-03
1500	41.609	.4476-03
1515	44.715	.4300-03
1530	47.820	.4113-03
1545	50.922	.3914-03
1600	54.017	.3709-03
1615	57.151	.3478-03
1630	60.172	.3201-03
1645	63.226	.2869-03
1700	66.262	.2493-03
1715	69.275	.2092-03
1730	72.263	.1683-03
1745	75.223	.1290-03
1800	78.152	.9361-04
1815	81.045	.6434-04
1830	83.898	.3391-04
1845	86.707	.1538-04
1900	89.469	.0000
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.343	.0000
2030	104.699	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued)

SPECIES: HNO3

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

Z (ZENITH ANGLE) (DEGREES)	F (RATE CONSTANT) (/SEC)
.00	.5253-06
10.00	.5156-06
20.00	.4710-06
30.00	.4013-06
40.00	.3152-06
50.00	.2083-06
60.00	.1112-06
70.00	.3813-07
78.00	.3806-08
86.00	.5945-09

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.950	.0000
445	90.239	.0000
500	87.513	.1537-09
515	84.717	.1516-08
530	81.876	.3405-08
545	78.994	.6973-08
600	76.075	.1343-07
615	73.124	.2345-07
630	70.144	.3736-07
645	67.137	.5535-07
700	64.108	.7706-07
715	61.058	.1020-06
730	57.992	.1295-06
745	54.911	.1590-06
800	51.819	.1899-06
815	48.719	.2216-06
830	45.614	.2535-06
845	42.508	.2851-06
900	39.405	.3160-06
915	36.311	.3456-06
930	33.232	.3736-06
945	30.178	.3996-06
1000	27.159	.4232-06
1015	24.195	.4444-06
1030	21.312	.4631-06
1045	18.559	.4793-06
1100	15.977	.4927-06
1115	13.704	.5029-06
1130	11.905	.5097-06
1145	10.823	.5133-06
1200	10.678	.5137-06
1215	11.507	.5111-06
1230	13.124	.5052-06
1245	15.252	.4960-06
1300	17.782	.4835-06
1315	20.497	.4680-06
1330	23.350	.4500-06
1345	26.294	.4296-06
1400	29.299	.4067-06
1415	32.345	.3814-06
1430	35.418	.3539-06
1445	38.508	.3247-06
1500	41.609	.2942-06
1515	44.715	.2627-06
1530	47.820	.2309-06
1545	50.922	.1991-06
1600	54.017	.1679-06
1615	57.104	.1379-06
1630	60.172	.1097-06
1645	63.226	.8398-07
1700	66.262	.6128-07
1715	69.275	.4215-07
1730	72.263	.2707-07
1745	75.223	.1595-07
1800	78.152	.8503-08
1815	81.045	.4214-08
1830	83.898	.1960-08
1845	86.797	.5583-09
1900	89.469	.0000
1915	92.176	.0000
1930	94.823	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.343	.0000
2030	104.691	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued)

SPECIES: O33P

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

Z (ZENITH ANGLE) (DEGREES)	J (RATE CONSTANT) (/SEC)
.90	.5513-03
10.90	.5477-03
20.90	.5357-03
30.90	.5135-03
40.90	.4820-03
50.90	.4413-03
60.90	.3791-03
70.90	.2842-03
78.90	.1578-03
86.90	.2698-04

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.569	.0000
430	92.950	.0000
445	90.259	.0000
500	87.513	.0000
515	84.717	.5025-04
530	81.876	.1012-03
545	78.994	.1512-03
600	76.075	.1989-03
615	73.124	.2430-03
630	70.144	.2824-03
645	67.137	.3165-03
700	64.108	.3457-03
715	61.058	.3710-03
730	57.992	.3936-03
745	54.911	.4139-03
800	51.819	.4319-03
815	48.719	.4475-03
830	45.614	.4610-03
845	42.508	.4730-03
900	39.405	.4841-03
915	36.311	.4945-03
930	33.232	.5042-03
945	30.178	.5130-03
1000	27.159	.5208-03
1015	24.195	.5276-03
1030	21.312	.5334-03
1045	18.550	.5381-03
1100	15.977	.5418-03
1115	13.704	.5444-03
1130	11.905	.5462-03
1145	10.823	.5471-03
1200	10.679	.5472-03
1215	11.507	.5465-03
1230	13.124	.5450-03
1245	15.282	.5426-03
1300	17.782	.5393-03
1315	20.497	.5349-03
1330	23.350	.5294-03
1345	26.294	.5229-03
1400	29.299	.5154-03
1415	32.345	.5068-03
1430	35.418	.4973-03
1445	38.508	.4871-03
1500	41.609	.4763-03
1515	44.715	.4646-03
1530	47.820	.4516-03
1545	50.922	.4366-03
1600	54.017	.4194-03
1615	57.101	.3998-03
1630	60.172	.3778-03
1645	63.226	.3534-03
1700	66.262	.3254-03
1715	69.275	.2929-03
1730	72.263	.2549-03
1745	75.223	.2121-03
1800	78.152	.1653-03
1815	81.044	.1159-03
1830	83.893	.6595-04
1845	86.707	.1414-04
1900	89.469	.0000
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.348	.0000
2030	104.690	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued)

SPECIES: 0310

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

Z (ZENITH ANGLE) (DEGREES)	K (RATE CONSTANT) (/SEC)
.00	.7022-04
10.00	.6845-04
20.00	.6219-04
30.00	.5266-04
40.00	.4038-04
50.00	.2665-04
60.00	.1416-04
70.00	.4806-05
78.00	.1103-05
86.90	.1121-06

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.950	.0000
445	90.259	.0000
500	87.513	.1986-07
515	84.717	.1894-06
530	81.876	.4253-06
545	78.994	.8734-06
600	76.075	.1685-05
615	73.124	.2948-05
630	70.144	.4708-05
645	67.137	.6994-05
700	64.108	.9766-05
715	61.058	.1296-04
730	57.992	.1652-04
745	54.911	.2036-04
800	51.819	.2441-04
815	48.719	.2858-04
830	45.614	.3281-04
845	42.508	.3702-04
900	39.405	.4116-04
915	36.311	.4515-04
930	33.232	.4894-04
945	30.178	.5246-04
1000	27.159	.5566-04
1015	24.195	.5854-04
1030	21.312	.6110-04
1045	18.550	.6334-04
1100	15.977	.6522-04
1115	13.704	.6665-04
1130	11.905	.6762-04
1145	10.823	.6811-04
1200	10.678	.6818-04
1215	11.507	.6781-04
1230	13.124	.6698-04
1245	15.282	.6568-04
1300	17.782	.6393-04
1315	20.497	.6179-04
1330	23.350	.5932-04
1345	26.294	.5653-04
1400	29.299	.5342-04
1415	32.345	.4999-04
1430	35.418	.4628-04
1445	38.508	.4234-04
1500	41.609	.3823-04
1515	44.715	.3404-04
1530	47.820	.2981-04
1545	50.922	.2561-04
1600	54.017	.2152-04
1615	57.101	.1761-04
1630	60.172	.1396-04
1645	63.226	.1065-04
1700	66.262	.7749-05
1715	69.275	.5317-05
1730	72.263	.3405-05
1745	75.223	.2002-05
1800	78.152	.1063-05
1815	81.044	.5266-06
1830	83.893	.2447-06
1845	86.797	.7023-07
1900	89.469	.0000
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.343	.0000
2030	104.690	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued) SPECIES: O3SD

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

Z (ZENITH ANGLE) (DEGREES)	K (RATE CONSTANT) (/SEC)
.00	.1205-03
10.00	.1182-03
20.00	.1099-03
30.00	.9676-04
40.00	.7920-04
50.00	.5843-04
60.00	.3658-04
70.00	.1676-04
78.00	.5676-05
86.00	.9020-06

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.930	.0000
445	90.239	.0000
500	87.513	.2549-06
515	84.717	.1449-05
530	81.876	.2832-05
545	78.994	.4797-05
600	76.075	.7733-05
615	73.124	.1170-04
630	70.144	.1651-04
645	67.137	.2198-04
700	64.108	.2795-04
715	61.058	.3432-04
730	57.992	.4093-04
745	54.911	.4767-04
800	51.819	.5446-04
815	48.719	.6121-04
830	45.614	.6782-04
845	42.508	.7422-04
900	39.403	.8035-04
915	36.311	.8614-04
930	33.232	.9154-04
945	30.178	.9649-04
1000	27.159	.1009-03
1015	24.195	.1049-03
1030	21.312	.1084-03
1045	18.550	.1114-03
1100	15.977	.1139-03
1115	13.704	.1158-03
1130	11.905	.1171-03
1145	10.823	.1177-03
1200	10.678	.1178-03
1215	11.507	.1173-03
1230	13.124	.1163-03
1245	15.282	.1145-03
1300	17.782	.1122-03
1315	20.497	.1093-03
1330	23.350	.1060-03
1345	26.294	.1021-03
1400	29.299	.9783-04
1415	32.345	.9302-04
1430	35.418	.8775-04
1445	38.508	.8207-04
1500	41.609	.7603-04
1515	44.715	.6970-04
1530	47.820	.6314-04
1545	50.922	.5643-04
1600	54.017	.4964-04
1615	57.101	.4287-04
1630	60.172	.3621-04
1645	63.226	.2976-04
1700	66.262	.2366-04
1715	69.275	.1803-04
1730	72.263	.1301-04
1745	75.223	.8783-05
1800	78.152	.5533-05
1815	81.044	.3324-05
1830	83.898	.1813-05
1845	86.707	.6029-06
1900	89.469	.0000
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.348	.0000
2030	104.690	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued)

SPECIES: FOR1

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

Z (ZENITH ANGLE) (DEGREES)	(RATE CONSTANT) (/SEC)
.00	.3565-04
10.00	.3517-04
20.00	.3354-04
30.00	.3078-04
40.00	.2681-04
50.00	.2158-04
60.00	.1531-04
70.00	.8213-05
78.00	.3354-05
86.00	.6446-06

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.950	.0000
445	90.259	.0000
500	87.513	.2252-06
515	84.717	.9994-06
530	81.876	.1848-05
545	78.994	.2914-05
600	76.075	.4335-05
615	73.124	.6106-05
630	70.144	.8113-05
645	67.137	.1024-04
700	64.108	.1242-04
715	61.058	.1458-04
730	57.992	.1666-04
745	54.911	.1864-04
800	51.819	.2052-04
815	48.719	.2231-04
830	45.614	.2402-04
845	42.508	.2561-04
900	39.405	.2709-04
915	36.311	.2843-04
930	33.232	.2964-04
945	30.178	.3072-04
1000	27.159	.3168-04
1015	24.195	.3252-04
1030	21.312	.3324-04
1045	18.550	.3385-04
1100	15.977	.3435-04
1115	13.704	.3471-04
1130	11.905	.3496-04
1145	10.823	.3508-04
1200	10.678	.3510-04
1215	11.507	.3501-04
1230	13.124	.3480-04
1245	15.282	.3446-04
1300	17.782	.3401-04
1315	20.497	.3343-04
1330	23.350	.3274-04
1345	26.294	.3193-04
1400	29.299	.3101-04
1415	32.345	.2996-04
1430	35.418	.2879-04
1445	38.508	.2749-04
1500	41.609	.2605-04
1515	44.715	.2449-04
1530	47.820	.2282-04
1545	50.922	.2105-04
1600	54.017	.1919-04
1615	57.101	.1724-04
1630	60.172	.1519-04
1645	63.226	.1305-04
1700	66.262	.1087-04
1715	69.275	.8721-05
1730	72.263	.6668-05
1745	75.223	.4817-05
1800	78.152	.3284-05
1815	81.044	.2128-05
1830	83.898	.1232-05
1845	86.707	.4497-06
1900	89.469	.0000
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.348	.0000
2030	104.690	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued)

SPECIES: FOR2

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

Z (ZENITH ANGLE) (DEGREES)	K (RATE CONSTANT) (/SEC)
.00	.9327-04
10.00	.9221-04
20.00	.8884-04
30.00	.8298-04
40.00	.7425-04
50.00	.6212-04
60.00	.4736-04
70.00	.2692-04
78.00	.1194-04
86.00	.2521-05

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.950	.0000
445	90.259	.0000
500	87.513	.9798-06
515	84.717	.3826-05
530	81.876	.6879-05
545	78.994	.1050-04
600	76.075	.1506-04
615	73.124	.2053-04
630	70.144	.2661-04
645	67.137	.3301-04
700	64.108	.3939-04
715	61.058	.4542-04
730	57.992	.5078-04
745	54.911	.5547-04
800	51.819	.5973-04
815	48.719	.6379-04
830	45.614	.6773-04
845	42.508	.7147-04
900	39.405	.7487-04
915	36.311	.7788-04
930	33.232	.8053-04
945	30.178	.8285-04
1000	27.159	.8490-04
1015	24.195	.8668-04
1030	21.312	.8821-04
1045	18.550	.8949-04
1100	15.977	.9051-04
1115	13.704	.9127-04
1130	11.905	.9178-04
1145	10.823	.9204-04
1200	10.678	.9207-04
1215	11.507	.9188-04
1230	13.124	.9144-04
1245	15.282	.9076-04
1300	17.782	.8981-04
1315	20.497	.8861-04
1330	23.350	.8715-04
1345	26.294	.8544-04
1400	29.299	.8347-04
1415	32.345	.8123-04
1430	35.418	.7868-04
1445	38.508	.7578-04
1500	41.609	.7249-04
1515	44.715	.6884-04
1530	47.820	.6495-04
1545	50.922	.6091-04
1600	54.017	.5674-04
1615	57.101	.5219-04
1630	60.172	.4705-04
1645	63.226	.4119-04
1700	66.262	.3487-04
1715	69.275	.2845-04
1730	72.263	.2224-04
1745	75.223	.1656-04
1800	78.152	.1171-04
1815	81.044	.7853-05
1830	83.898	.4674-05
1845	86.707	.1803-05
1900	89.469	.0000
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.348	.0000
2030	104.690	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued)

SPECIES: H2O2

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

(ZENITH ANGLE) (DEGREES)	K (RATE CONSTANT) (/SEC)
.00	.2717-04
10.00	.2685-04
20.00	.2580-04
30.00	.2401-04
40.00	.2138-04
50.00	.1778-04
60.00	.1344-04
70.00	.7634-05
78.00	.3370-05
86.00	.7076-06

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.950	.0000
445	90.259	.0000
500	87.513	.0000
515	84.717	.2741-06
530	81.876	.1075-05
545	78.994	.1935-05
600	76.075	.2961-05
615	73.124	.4257-05
630	70.144	.5817-05
645	67.137	.7549-05
700	64.108	.9360-05
715	61.058	.1116-04
730	57.992	.1288-04
745	54.911	.1443-04
800	51.819	.1580-04
815	48.719	.1707-04
830	45.614	.1827-04
845	42.508	.1944-04
900	39.405	.2055-04
915	36.311	.2156-04
930	33.232	.2247-04
945	30.178	.2326-04
1000	27.159	.2397-04
1015	24.195	.2460-04
1030	21.312	.2514-04
1045	18.550	.2561-04
1100	15.977	.2600-04
1115	13.704	.2632-04
1130	11.905	.2656-04
1145	10.823	.2671-04
1200	10.678	.2679-04
1215	11.507	.2680-04
1230	13.124	.2674-04
1245	15.282	.2661-04
1300	17.782	.2640-04
1315	20.497	.2610-04
1330	23.350	.2573-04
1345	26.294	.2529-04
1400	29.299	.2476-04
1415	32.345	.2416-04
1430	35.418	.2348-04
1445	38.508	.2271-04
1500	41.609	.2183-04
1515	44.715	.2085-04
1530	47.820	.1977-04
1545	50.922	.1862-04
1600	54.017	.1742-04
1615	57.101	.1618-04
1630	60.172	.1484-04
1645	63.226	.1335-04
1700	66.262	.1167-04
1715	69.275	.9887-05
1730	72.263	.8069-05
1745	75.223	.6305-05
1800	78.152	.4686-05
1815	81.044	.3305-05
1830	83.898	.2210-05
1845	86.707	.1313-05
1900	89.469	.5058-06
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.348	.0000
2030	104.690	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued) SPECIES: ACA1

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

Z (ZENITH ANGLE) (DEGREES)	K (RATE CONSTANT) (/SEC)
.00	.7084-05
10.00	.6966-05
20.00	.6549-05
30.00	.5857-05
40.00	.4902-05
50.00	.3717-05
60.00	.2394-05
70.00	.1129-05
78.00	.3860-06
86.00	.6023-07

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.950	.0000
445	90.259	.0000
500	87.513	.1596-07
515	84.717	.9763-07
530	81.876	.1922-06
545	78.994	.3261-06
600	76.075	.5258-06
615	73.124	.7932-06
630	70.144	.1113-05
645	67.137	.1469-05
700	64.108	.1852-05
715	61.058	.2253-05
730	57.992	.2663-05
745	54.911	.3075-05
800	51.819	.3483-05
815	48.719	.3880-05
830	45.614	.4261-05
845	42.508	.4624-05
900	39.405	.4966-05
915	36.311	.5284-05
930	33.232	.5577-05
945	30.178	.5843-05
1000	27.159	.6080-05
1015	24.195	.6290-05
1030	21.312	.6473-05
1045	18.550	.6628-05
1100	15.977	.6754-05
1115	13.704	.6849-05
1130	11.905	.6912-05
1145	10.823	.6945-05
1200	10.678	.6949-05
1215	11.507	.6925-05
1230	13.124	.6871-05
1245	15.282	.6785-05
1300	17.782	.6668-05
1315	20.497	.6521-05
1330	23.350	.6346-05
1345	26.294	.6144-05
1400	29.299	.5914-05
1415	32.345	.5657-05
1430	35.418	.5372-05
1445	38.508	.5061-05
1500	41.609	.4726-05
1515	44.715	.4368-05
1530	47.820	.3992-05
1545	50.922	.3599-05
1600	54.017	.3194-05
1615	57.101	.2782-05
1630	60.172	.2371-05
1645	63.226	.1966-05
1700	66.262	.1578-05
1715	69.275	.1213-05
1730	72.263	.8811-06
1745	75.223	.5969-06
1800	78.152	.3763-06
1815	81.044	.2257-06
1830	83.898	.1226-06
1845	86.707	.3976-07
1900	89.469	.0000
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.348	.0000
2030	104.690	.0000
2045	106.936	.0000
2100	109.075	.0000

(continued)

TABLE 2. (continued)

SPECIES: ACA2

INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS:

Z (ZENITH ANGLE) (DEGREES)	K (RATE CONSTANT) (/SEC)
.00	.1503-06
10.00	.1459-06
20.00	.1310-06
30.00	.1089-06
40.00	.8116-07
50.00	.5197-07
60.00	.2625-07
70.00	.8581-08
78.00	.1921-08
86.00	.1951-09

TIME (LOCAL STANDARD)	ZENITH ANGLE (DEGREES)	RATE CONSTANT (/SEC)
400	98.142	.0000
415	95.580	.0000
430	92.950	.0000
445	90.259	.0000
500	87.513	.3889-10
515	84.717	.3261-09
530	81.876	.7316-09
545	78.994	.1516-08
600	76.075	.2950-08
615	73.124	.5210-08
630	70.144	.8402-08
645	67.137	.1261-07
700	64.108	.1781-07
715	61.058	.2393-07
730	57.992	.3090-07
745	54.911	.3860-07
800	51.819	.4689-07
815	48.719	.5561-07
830	45.614	.6463-07
845	42.508	.7377-07
900	39.405	.8290-07
915	36.311	.9184-07
930	33.232	.1004-06
945	30.178	.1085-06
1000	27.159	.1158-06
1015	24.195	.1225-06
1030	21.312	.1285-06
1045	18.550	.1338-06
1100	15.977	.1382-06
1115	13.704	.1416-06
1130	11.905	.1439-06
1145	10.823	.1451-06
1200	10.678	.1453-06
1215	11.507	.1444-06
1230	13.124	.1424-06
1245	15.282	.1393-06
1300	17.782	.1351-06
1315	20.497	.1301-06
1330	23.350	.1243-06
1345	26.294	.1178-06
1400	29.299	.1107-06
1415	32.345	.1028-06
1430	35.418	.9437-07
1445	38.508	.8551-07
1500	41.609	.7642-07
1515	44.715	.6727-07
1530	47.820	.5820-07
1545	50.922	.4938-07
1600	54.017	.4094-07
1615	57.101	.3306-07
1630	60.172	.2586-07
1645	63.226	.1949-07
1700	66.262	.1402-07
1715	69.275	.9516-08
1730	72.263	.6034-08
1745	75.223	.3515-08
1800	78.152	.1853-08
1815	81.044	.9078-09
1830	83.898	.4203-09
1845	86.707	.1244-09
1900	89.469	.0000
1915	92.176	.0000
1930	94.824	.0000
1945	97.407	.0000
2000	99.917	.0000
2015	102.348	.0000
2030	104.690	.0000
2045	106.936	.0000
2100	109.075	.0000

These data and those from similar program listings for March 21 and December 21 have been incorporated into Figures 3, 4, and 5, which show the seasonal variations in the diurnal rate constant curves for three photolytic reactions. These include the formation of NO and $O(^3P)$ from the photolysis of NO_2, $O(^1D)$ and O_2 formation from O_3 photolysis, and HCO and H formation from CH_2O photolysis respectively.

The large seasonal variation in the rate constant for the given O_3 photolysis reaction as compared to the other two reactions is immediately apparent. This sensitivity is a consequence of the photolysis process occurring in the wavelength region $\lambda < 310$nm. Figure 6, from Peterson[9], depicts the normal

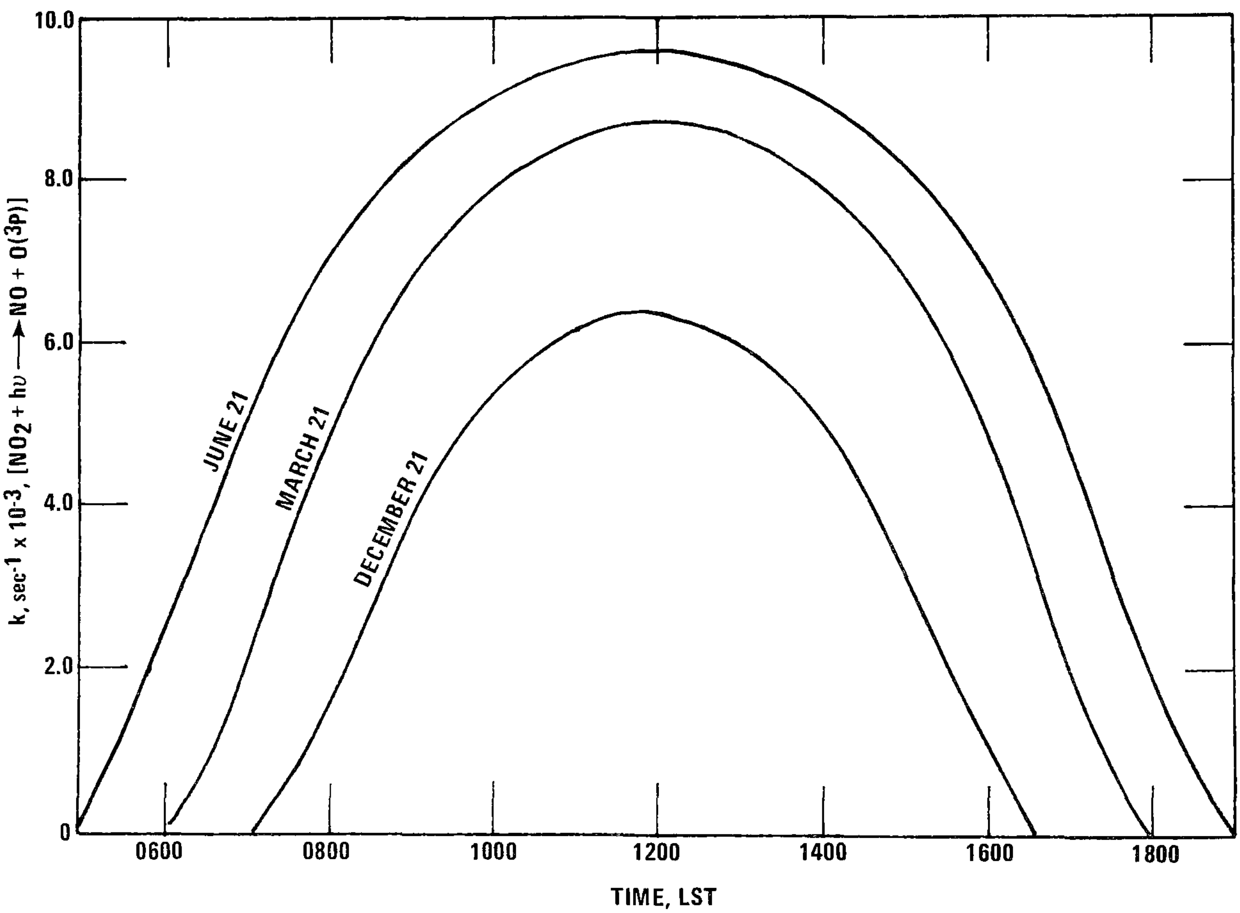

Figure 3. Diurnal variation of the photolytic rate constant for the formation of $O(^3P)$ from NO_2 in Los Angeles (34.1°N, 118.3°W) for three times of the year.

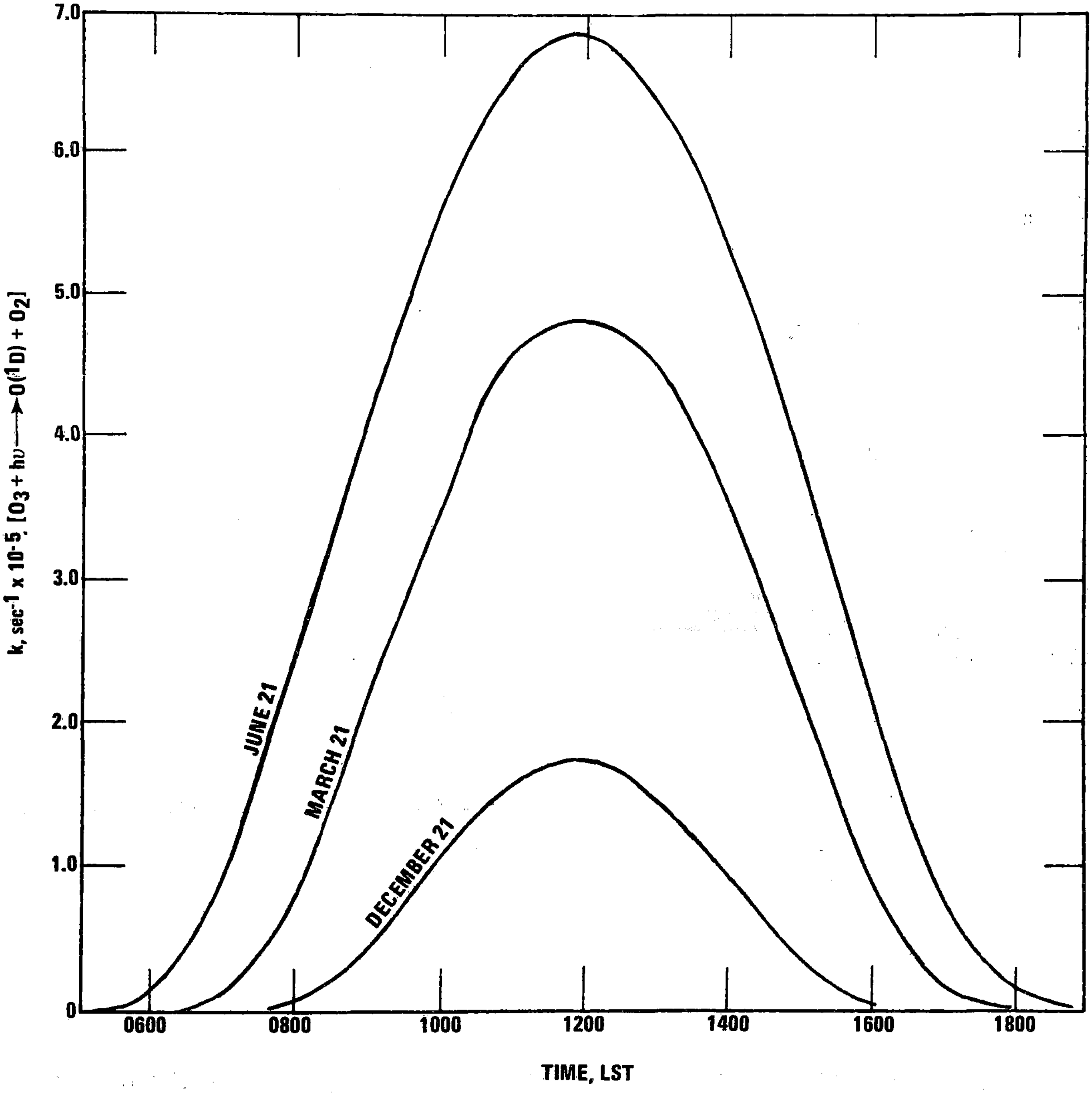

Figure 4. Diurnal variation of the photolytic rate constant for the formation of $O(^1D)$ from O_3 in Los Angeles (34.1°N, 118.3°W) for three times of the year.

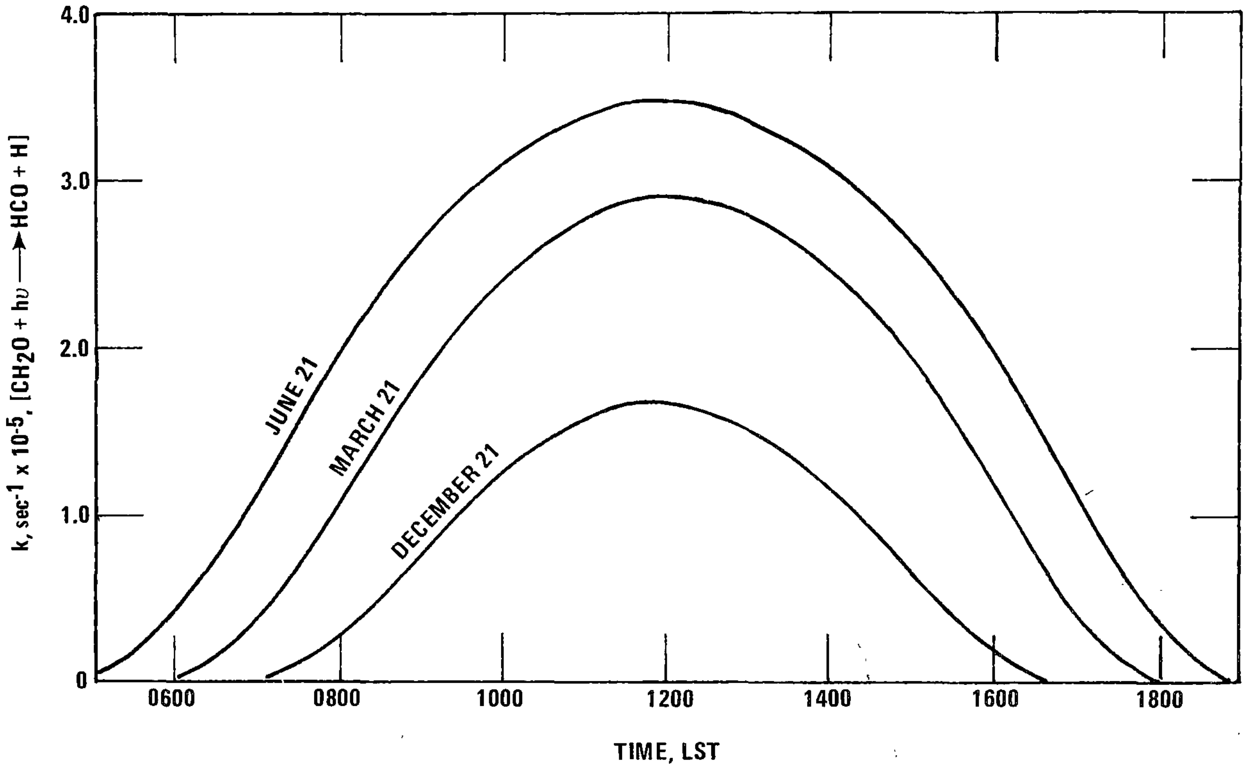

Figure 5. Diurnal variation of the photolytic rate constant for the formation of HCO or H from CH_2O in Los Angeles (34.1°N, 118.3°W) for three times of the year.

optical thickness (NOT), a measure of the extinction of the direct solar beam by the atmosphere, as a function of wavelength for a zenith angle of 0^o. The normal optical thickness is described by the equation

$$NOT = \int_0^{z_{top}} k_\lambda \rho \, dz \quad (21)$$

where k_λ is a wavelength-dependent extinction coefficient, ρ is the density of the absorbing medium, and z_{top} represents the top of the atmosphere[22]. In the wavelength region from 290 to 310nm the optical thickness is completely dominated by the effects of ozone absorption and Rayleigh scattering. From Beer's Law, the intensity of the transmitted radiation, I_T, is given by

$$I_T = I_o \, e^{-a(NOT)} \quad (22)$$

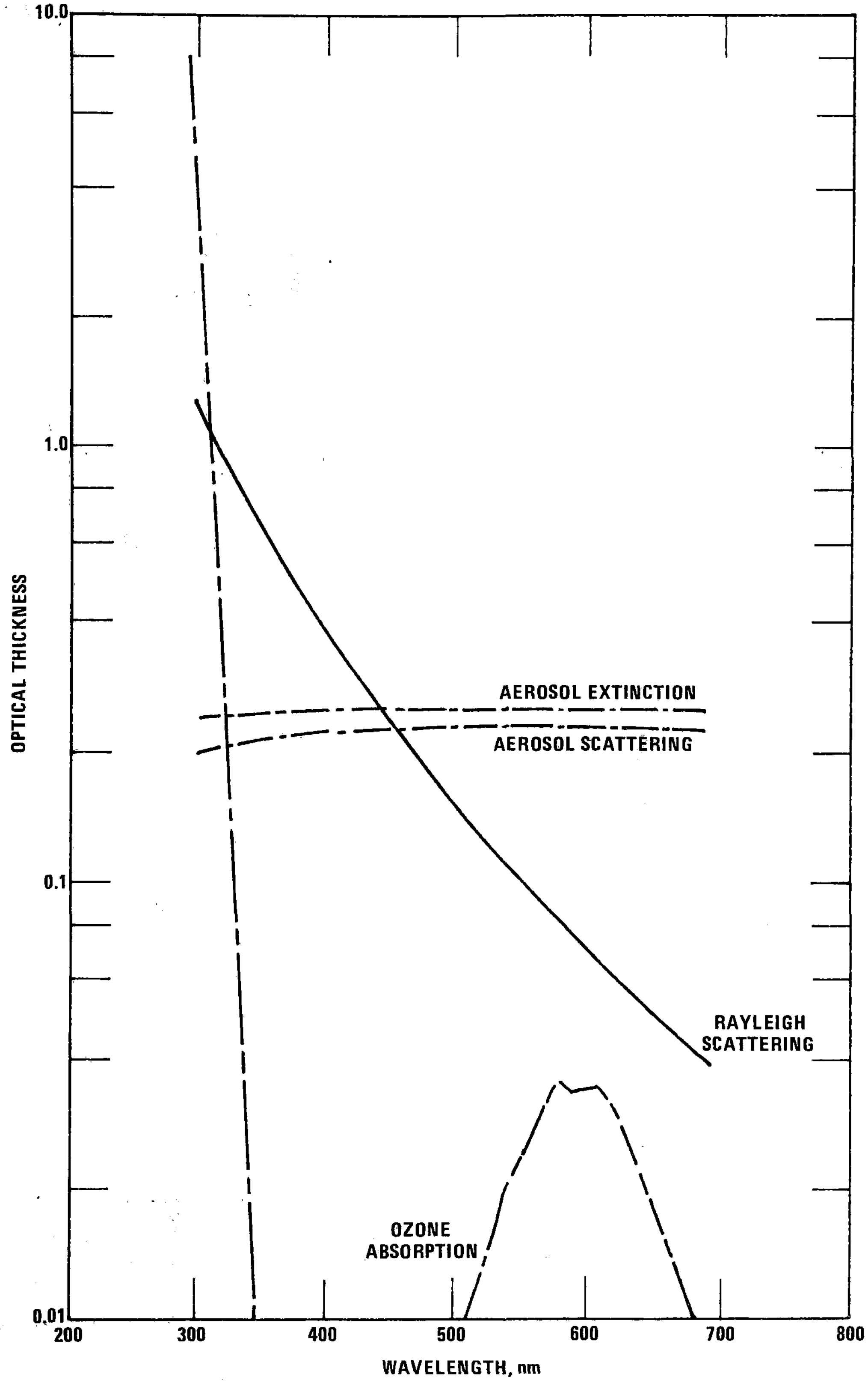

Figure 6. Normal optical thickness for a zenith angle of 0^{o} as a function of wavelength (nm) for aerosol scattering and extinction, Rayleigh scattering, and ozone absorption (from Peterson[8]).

where I_0 is the light intensity at the top of the atmosphere and a is the optical air mass, the length of the path of light through the atmosphere as a multiple of that from a source at a zenith angle of 0^o (a=1). At larger zenith angles the optical air mass increases by a factor ranging from 1.02 at 10^o, 1.56 at 50^o, 4.72 at 78^o, to 12.4 at 86^o [9].

The transmitted radiation, therefore, shows greater sensitivity to variations in solar zenith angle at the shorter wavelengths. This is a result of the exponential dependence of I_T on optical air mass and total atmospheric extinction. Hence, the December curve in Figure 4 for $O(^1D)$ production from ozone is proportionately more depressed than are the winter curves for other reactions. This is due to the larger zenith angles occurring throughout the day at this time of the year and also to ozone's absorption at wavelengths less than 310nm.

SECTION VI

THEORETICAL RESULTS AND EXPERIMENTAL OBSERVATIONS

To test the applicability of the computed photolytic rate constants to a realistic ambient atmospheric situation, a comparison was made between the computed results and observed rate constants. Until relatively recently direct measurement of photolytic rate constants has been cumbersome, if not impossible. Of late, however, a device has been designed and built which provides a continuous in situ measurment of the rate constant (k_{NO_2}) for the photolysis of NO_2[23]. The device consists of a 1-liter round bottom quartz flask through which nitrogen dioxide is pumped. When the flask is placed in sunlight the NO_2 photolyzes into NO and O. The concentrations of NO and NO_2 are frequently monitored, and from these measurements k_{NO_2} is readily calculated. The device was operative at Research Triangle Park, N.C. over a period of several days in late April 1975. Research Triangle Institute, under contract with the Environmental Protection Agency, conducted the project. During this time a variety of meteorological conditions prevailed over the area.

Since the photolytic rate constants generated by the program are applicable only to clear-sky conditions a method of relating them to conditions when clouds were present was formulated. The experimental k_{NO_2} data were primarily dependent on light absorption in the ultraviolet wavelength range. Thus, it was decided to scale the program-generated values by the simultaneous measurements of ultraviolet (UV) radiation at Research Triangle Park. The percentage departure of the UV measurements from their expected values during cloudless sky conditions were used to scale the rate constants from their clear-sky values. In this manner the rate constants for NO_2 photolysis directly measured at RTP were compared to those calculated by the program described here. Figures 7, 8, 9 and 10 present these comparisons.

Only one day for which data were available contained a period of time in which clear-sky conditions prevailed. This occurred from approximately sunrise until 1100 on April 27, 1975. Figure 7 presents the comparison for this day. The clear-sky and UV-scaled plots of k_{NO_2} are coincident here until 1100 when a cloud cover began to obscure the sky. After this point the UV-scaled portion of the plot deviates from the clear-sky case according to the UV attenuation factor. Figures 8 and 9 depict the results from two days within the experimental period during which time varying degrees of cloud cover prevailed over the region. Finally, Figure 10 shows the comparison for a day with completely overcast skies and some rain during the morning hours.

In all cases the observations of k_{NO_2} were averaged over 10-minute intervals. The UV scaling factors for the k_{NO_2} plot were computed over a comparable time period. Generally the observations and the UV-scaled plot of k_{NO_2} are in quite close agreement. There are, however, several exceptions that should be noted. The measured k_{NO_2} values for a large portion of the day on April 27, 1975, shown in Figure 7, are lower than the UV-scaled values by as much as 27% at 1000. This difference may possibly be understood by examining certain characteristics of the spherical-quartz flask measuring device. This type of system requires thorough mixing for maximum efficiency of NO_2 conversion. Moreover, the k_{NO_2} value measured from the spherical reactor was found to be flow dependent, yielding higher values at higher flow rates[24]. Thus, a mixing or flow problem, or both, may have held the measured k_{NO_2} values below expected levels here.

Figures 8, 9, and 10 show a less pronounced difference between measured and UV-scaled k_{NO_2} values. However, there does seem to exist a small, yet systematic, deviation in the morning hours as compared to the very close agreement in the afternoon. It has been noted that aerosol present in the atmosphere in higher concentrations during the morning hours tended to reduce the UV intensity, and hence the k_{NO_2} measured values[24]. The relative effects of higher aerosol concentrations on the UV radiometer and the k_{NO_2} reactor device may not be linear, causing a difference to exist between the observed and UV-scaled K_{NO_2} values. Lower temperatures also tended to reduce the values of

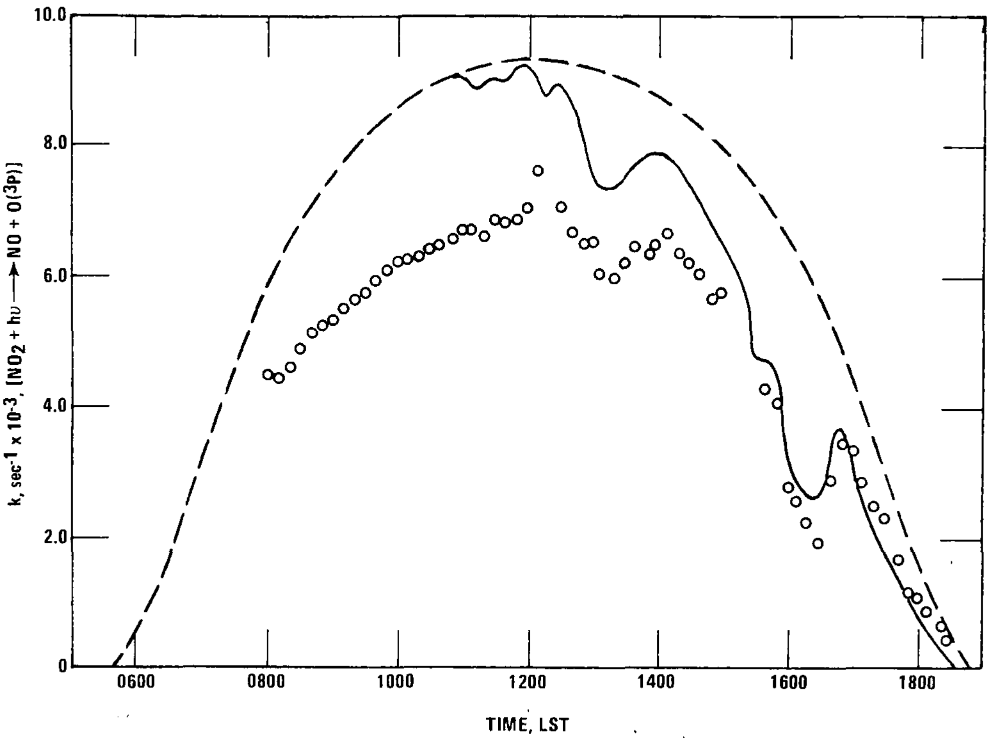

Figure 7. Comparison of the experimental (circles), theoretical (dashed line), and U.V.-scaled theoretical (solid line) diurnal variation of the photolytic rate constant for the photolysis of NO_2 near Raleigh, N.C. (35.8°N, 78.6°W) on April 27, 1975.

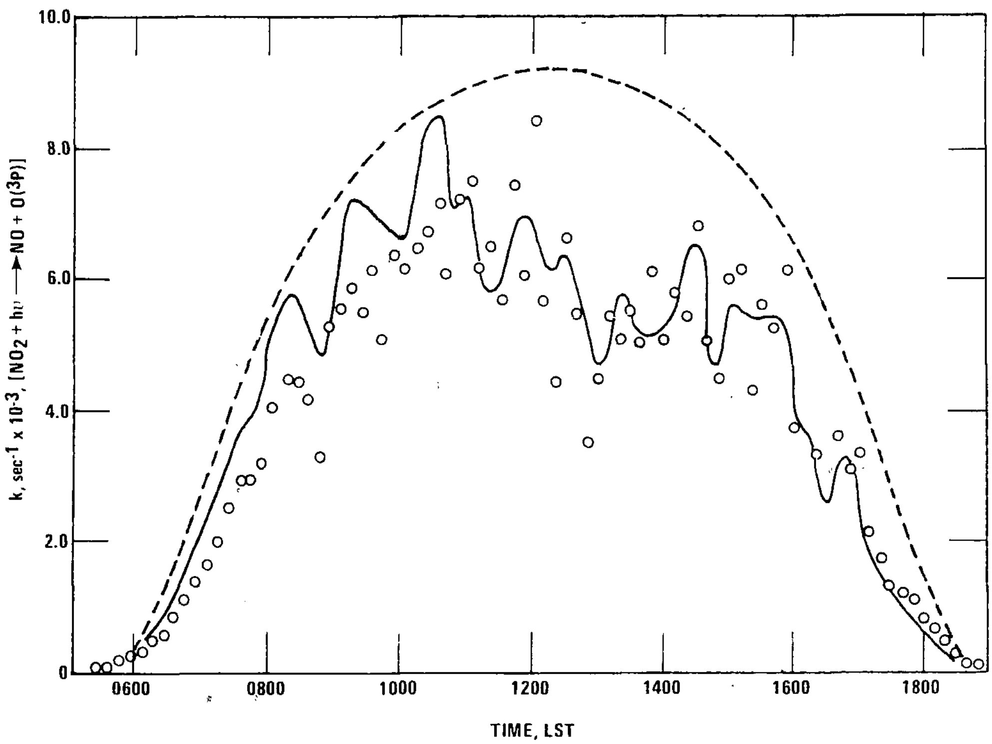

Figure 8. Comparison of the experimental (circles), theoretical (dashed line), and U.V.-scaled theoretical (solid line) diurnal variation of the photolytic rate constant for the photolysis of NO_2 near Raleigh, N.C. (35.8°N, 78.6°W) on April 23, 1975.

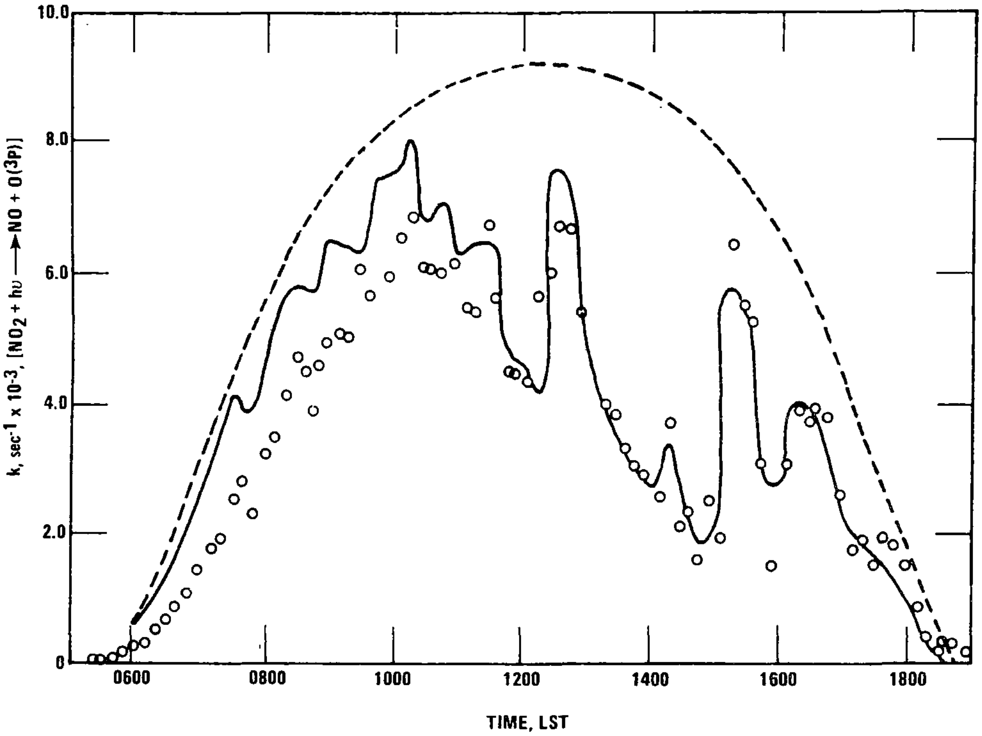

Figure 9. Comparison of the experimental (circles), theoretical (dashed line), and U.V.-scaled theoretical (solid line) diurnal variation of the photolytic rate constant for the photolysis of NO_2 near Raleigh, N.C. (35.8°N, 78.6°W) on April 25, 1975.

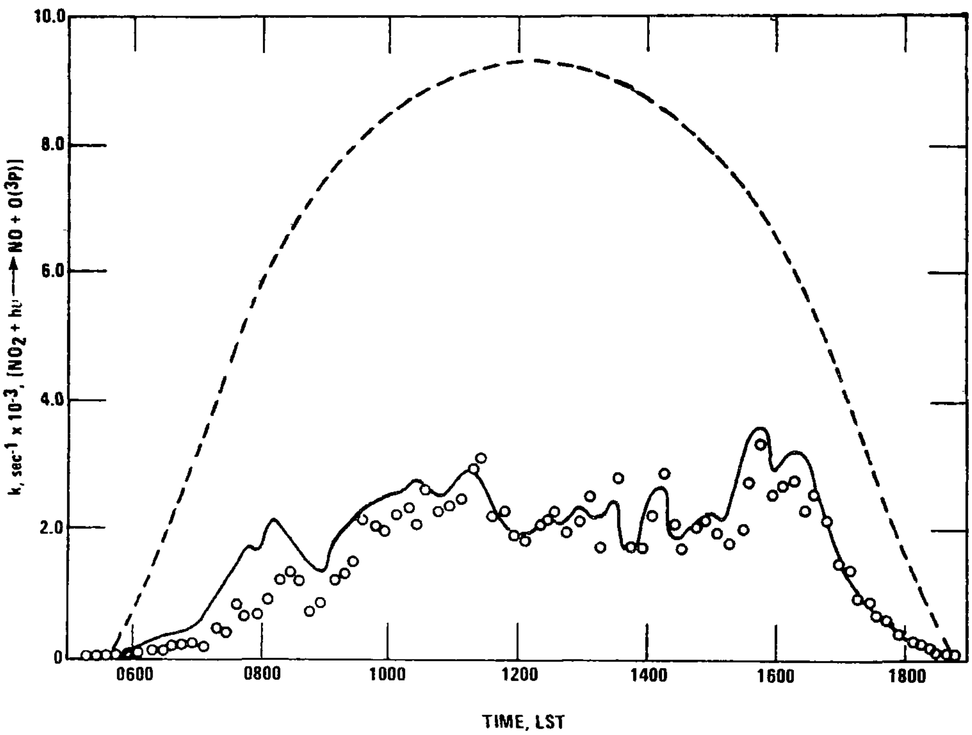

Figure 10. Comparison of the experimental (circles), theoretical (dashed line), and U.V.-scaled theoretical (solid line) diurnal variation of the photolytic rate constant for the photolysis of NO_2 near Raleigh, N.C. (35.8°N, 78.6°W) on April 28, 1975.

k_{NO_2} measured by the reactor mechanism[23]. This may also help account for the slight systematic difference seen in the morning.

The difference between theoretical clear-sky and observed (or scaled) k_{NO_2} values can be substantial, amounting to over 90% in the most overcast-sky situation. However, even in this case the UV-scaled theoretical values match the observations quite well as figure 10 shows. Implicitly, the program-generated photolytic rate constants are accurate in themselves for use in a photochemical kinetic mechanism as applied to clear-sky conditions. Should they be utilized in such a mechanism for other than clear-sky conditions it is apparent that some method of scaling the values, such as the one used here, is necessary. The full treatment of the attenuation of the solar radiation by fluctuations in cloud cover is beyond the scope of this work.

SECTION VII

SUMMARY AND CONCLUSIONS

The generation of the diurnal variation of photolytic rate constants by a computer program based on their theoretical formulation has been shown. These rate constants may be computed for a specific location and time given inputs of latitude, longitude, date, and local standard time. At present, the program generates rate constants applicable to the lower atmospheric photodissociation of NO_2, O_3, HONO, $HONO_2$, H_2CO, CH_3CHO, and H_2O_2.

Comparisons between observed and theoretical rate constant values for the photolysis of NO_2 in the real atmosphere show good agreement in clear-sky conditions and in cloudy-sky situations when the theoretical values are scaled by a UV attenuation factor. The diurnal variation in the photolytic rate constants produced by the program provides a tractable method for including this daily cycle in a chemical kinetic mechanism that may run through many hours of the day.

Integration of a relatively simple method of treating the solar radiation attenuation by varying amounts of cloud cover into the routine would provide greater flexibility in the application of the program. This constitutes the major suggestion for further research on the topic.

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ADDENDUM

During the final preparation of this report, new experimental data on the absorption cross section for nitrogen dioxide were reported by Bass, Ledford and Laufer[1] at the National Bureau of Standards.

It is recommended that these cross section data be used in place of those currently available in the computer algorithm, which are based on the work of Hall and Blacet[2]. The recommended averaged NO_2 cross section data are as follows:

nm	σ $cm^2 X 10^{20}$	nm	σ $cm^2 X 10^{20}$
290	8.52	380	56.99
300	12.83	390	58.22
310	18.26	400	59.52
320	24.74	410	58.03
330	30.95	420	(54.52)
340	37.39	430	(51.46)
350	44.90	440	(48.48)
360	50.11	450	(45.51)
370	54.05		

These new data represent approximately a thirteen percent reduction in the nitrogen dioxide cross sections currently in use. The Bass et al. work did not extend the measurements beyond 410 nm and therefore the values reported in parenthesis are estimates based on extrapolating the averaged percentage reduction between the Bass et al. and Hall and Blacet cross sections to the Hall and Blacet averaged values at 420, 430, 440 and 450nm.

The calculated photolytic rate constant for nitrogen dioxide dissociation using the Bass et al. cross section at ten zenith angles is given below.

Z degrees	k_{NO_2} seconds^{-1}
0.0	8.548×10^{-3}
10.0	8.478×10^{-3}
20.0	8.271×10^{-3}
30.0	7.900×10^{-3}
40.0	7.325×10^{-3}
50.0	6.468×10^{-3}
60.0	5.281×10^{-3}
70.0	3.431×10^{-3}
78.0	1.691×10^{-3}
86.0	3.635×10^{-4}

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APPENDIX A

LISTING OF COMPUTER PROGRAM CODE

On the following pages the FORTRAN code for the computer program is listed. It is composed of a main segment, six subroutines, and one function. Although the program was developed and originally run on the UNIVAC 1110 at the National Computer Center in Research Triangle Park, N.C., the code is of a general nature so as to be easily adapted to most computer installations. The central processing time for an execution of the compiled program as listed here and run on the UNIVAC 1110 is approximately 5 seconds.

```
*RATECONSTANT.MAIN
      C
      C    ****    RATE CONSTANT CALCULATIONS FOR FIRST ORDER PHOTOCHEMICAL REACTIONS
      C
            REAL*8  K
            COMMON XJ(52,10),SIGMA(52,20),PHI(52,20),Z(10),RTCON(10)
            COMMON LAM1,INC,SLA,SLO,TZ,IY,IM,ID,ISTRT,ISTOP,IINC
            COMMON SPECIE,MAXZ,ITIME(100),XZ(100),K(100),JSTRT,JSTOP
            DIMENSION PLACE(6)
      C
      C    ****    INPUT LOCATION LATITUDE,LONGITUDE,TIME ZONE,DATE,
      C    ****        TIMES TO BEGIN AND END CALCULATIONS, AND TIME INCREMENT
      C
            READ(5,14) PLACE,SLA,SLO,TZ,IY,IM,ID,JSTRT,JSTOP,IINC
         14 FORMAT(6A4,5X,2F10.4,/,F5.1,4X,I4,4X,I2,4X,I2,/,3(I4,4X))
      C
      C    ****    INPUT NUMBER OF SPECIES, NUMBER OF ZENITH ANGLES,
      C    ****        NUMBER OF WAVELENGTH VALUES USED, INITIAL WAVELENGTH VALUE,
      C    ****        AND WAVELENGTH INCREMENT.
      C
            READ(5,100) MAXL, MAXZ, MAXJ, LAM1, INC
        100 FORMAT(5I4)
      C
      C    ****    INPUT VALUES OF ZENITH ANGLES
      C
            READ(5,105) (Z(I),I=1,MAXZ)
        105 FORMAT(20F4.0)
      C
      C
      C    ****    PRINT OUT HEADING
      C
            WRITE(6,112) PLACE,SLA,SLO,IM,ID,IY,JSTRT,JSTOP
        112 FORMAT('1',//////////,40X,'PHOTOLYTIC RATE CONSTANTS, K, FOR VARIO
           +US SPECIES AS',/,48X,'A FUNCTION OF TIME AND ZENITH ANGLE',/////,
           +40X,'LOCATION: ',6A4,//,40X,'LATITUDE: ',F10.3,//,40X,'LONGITUDE:
           +',F10.3,//,40X,'DATE: ',5X,3(I4,3X),//,40X,'TIME: ',5X,I4,5X,'TO',
           +5X,I4,5X,'LOCAL STANDARD TIME')
      C
      C    ****    INPUT VALUES OF ACTINIC IRRADIANCE (J) FOR THE CORRESPONDING
      C    ****        ZENITH ANGLES
      C
            DO  5 I=1,MAXJ
            READ(5,110)  (XJ(I,J), J=1,MAXZ)
        110 FORMAT(8F10.7,/,2F10.7)
          5 CONTINUE
      C
      C    ****    FOR EACH SPECIES INPUT THE SPECIES NUMBER, THE SPECIES NAME,
      C    ****        WAVELENGTH AT WHICH TO BEGIN SUMMATION, AND WAVELENGTH AT
      C    ****            WHICH TO STOP SUMMATION
      C
         10 READ(5,115) L,SPECIE, MINLAM,MAXLAM
        115 FORMAT(I2,2X,A4,2X,I4,2X,I4)
            ISTRT = (MINLAM-LAM1)/INC + 1
            ISTOP = (MAXLAM-LAM1)/INC + 1
      C
      C    ****    INPUT ABSORPTION COEFFICIENTS FOR EACH SPECIES
```

```
C
      READ(5,120) (SIGMA(I,L), I=ISTRT,ISTOP)
  120 FORMAT(5(10E8.2,/),2E8.2)
C
C    ****     INPUT QUANTUM YIELDS FOR EACH SPECIES
C
      READ(5,125)  (PHI(J,L), J=ISTRT,ISTOP)
  125 FORMAT(5(10F8.4,/),2F8.4)
      DO 15 M=1,MAXZ
C
C    ****     CALL SUBROUTINE TO CALCULATE RATE CONSTANTS
C
      CALL RATE(L,M,MINLAM,MAXLAM,RTCON(M))
   15 CONTINUE
C
C    ****     CALL SUBROUTINE FOR SPLINE INTERPOLATION OF RATE CONSTANTS
C
      CALL  INTERP

C
C    ****     CALL SUBROUTINE FOR PROGRAM OUTPUT
C
      CALL OUT
C
C    ****     TEST FOR LAST SPECIES
C
      IF(L.GE.MAXL)  STOP
      GO TO 10
      END
>
```

```
*RATECONSTANT.RATE
      SUBROUTINE RATE(L,NZ,MINLAM,MAXLAM,SUM)
      REAL*8   K
      COMMON XJ(52,10),SIGMA(52,20),PHI(52,20),Z(10),RTCON(10)
      COMMON LAM1,INC,SLA,SLO,TZ,IY,IM,ID,ISTRT,ISTOP,IINC
      COMMON SPECIE,MAXZ,ITIME(100),XZ(100),K(100),JSTRT,JSTOP
C
C    ****    THIS SUBROUTINE CALCULATES A SINGLE RATE CONSTANT ACCORDING TO
C    ****        THE GIVEN INPUTS
C
      SUM = 0.0
      DO 20 I=MINLAM,MAXLAM,INC
      II = (I-LAM1)/INC + 1
      SUM = SUM + XJ(II,NZ) * 1.0E+15 * SIGMA(II,L) * PHI(II,L)
   20 CONTINUE
      RETURN
      END
>
```

```
*RATECONSTANT.INTERP
      C
      C     ****     THIS SUBROUTINE COMPUTES INTERPOLATED VALUES OF RATE CONSTANTS
      C     ****         FOR PARTICULAR TIMES OF THE DAY AND ZENITH ANGLES
      C
            SUBROUTINE  INTERP
            REAL*8  K
            COMMON XJ(52,10),SIGMA(52,20),PHI(52,20),Z(10),RTCON(10)
            COMMON LAM1,INC,SLA,SLO,TZ,IY,IM,ID,ISTRT,ISTOP,IINC
            COMMON SPECIE,MAXZ,ITIME(100),XZ(100),K(100),JSTRT,JSTOP
            DIMENSION D(2),C(27),W(27),V(5),ZZ(10),TK(10)
            DATA D/0.0,0.0/
            NN=MAXZ
            DO 27 JP=1,NN
            ZZ(JP)=Z(JP)
            TK(JP)=RTCON(JP)
         27 CONTINUE
      C
      C     ****     CALL FIRST SUBROUTINE FOR SPLINE INTERPOLATION OF RATE CONSTANTS
      C
            CALL SPLNA(NN,ZZ,TK,2,D,C,W)
            II = 0
            TIME = JSTRT
         50 II = II+1
            XC=0.0
      C
      C     ****     CALL SUBROUTINE TO COMPUTE ZENITH ANGLES FROM TIME OF DAY
      C
            CALL SOLAR(SLA,SLO,TZ,IY,IM,ID,TIME,XC,5)
            XD=90.-XC
            ITIME(II) = TIME
            XZ(II) =XD
            V(1) = XD
            IF(XD.GT.90.0) GO TO 20
      C
      C     ****     CALL SECOND SUBROUTINE IN SPLINE INTERPOLATION SCHEME
      C
            CALL SPLNB(NN,ZZ,TK,C,V)
            K(II) = V(2)
            IF(K(II).LT.0.0)   K(II)=0.0
            GO TO 25
         20 K(II) = 0.0
         25 T1 = TIME
            TIME = CLOCK(T1,IINC)
            NTIME = TIME
            IF(NTIME.GT.JSTOP)  GO TO 60
            GO TO 50
         60 RETURN
            END
```

```
*RATECONSTANT.OUT
C
C     ****    THIS SUBROUTINE PRINTS OUT ALL RELEVANT PARAMETERS
C
      SUBROUTINE  OUT
      REAL*8  K
      COMMON XJ(52,10),SIGMA(52,20),PHI(52,20),Z(10),RTCON(10)
      COMMON LAM1,INC,SLA,SLO,TZ,IY,IM,ID,ISTRT,ISTOP,IINC
      COMMON SPECIE,MAXZ,ITIME(100),XZ(100),K(100),JSTRT,JSTOP
      WRITE(6,100) SPECIE
  100 FORMAT('1',57X,'SPECIES: ',A4,////)
      WRITE(6,105)
  105 FORMAT(40X,'INITIAL DATA POINTS USED IN SUBSEQUENT CALCULATIONS: '
     +,//,40X,'Z (ZENITH ANGLE)',20X,'K (RATE CONSTANT)',/,43X,
     +'(DEGREES)',29X,'(/SEC)',/)
      DO 80 I=1,MAXZ
      WRITE(6,110) Z(I), RTCON(I)
  110 FORMAT(44X,F8.2,25X,E10.4)
   80 CONTINUE
      WRITE(6,115)
  115 FORMAT('0',///,28X,'TIME',25X,'ZENITH ANGLE',25X,'RATE CONSTANT',/
     +,23X,'(LOCAL STANDARD)',19X,'(DEGREES)',29X,'(/SEC)',/)
      A = JSTOP - JSTRT
      B = FLOAT((JSTOP-JSTRT)/100)
      IEND = (B + (A-B*100.)/60.) * FLOAT(60/IINC) + 1.
      DO 90 II=1,IEND
      WRITE(6,120)  ITIME(II),XZ(II),K(II)
  120 FORMAT(28X,I4,27X,F8.3,28X,E10.4)
   90 CONTINUE
      RETURN
      END
>
```

```
*RATECONSTANT.SOLAR
      SUBROUTINE SOLAR (SLA,SLO,TZ,IY,IM,ID,TIME,D,NV)
C***
C***     SLA...  LATITUDE (DEG)   SOUTH = MINUS
C***     SLO...  LONGITUDE (DEG)   EAST = MINUS
C***     TZ...  TIME ZONE
C***            ALSO INCLUDES FRACTION IF LOCAL TIME IS NOT
C***             STANDARD MERIDIAN TIME.  E.G. POONA, INDIA 5.5
C***     IY..  YEAR
C***     IM..  MONTH
C***     ID..  DAY
C***     TIME.. LOCAL STANDARD TIME IN HOURS AND MINUTES.
C***            1:30 PM = 1330  ** STANDARD TIME **
C***     D..  RETURNED VALUE
C***     NV..  VALUE TO BE RETURNED, SELECTED AS FOLLOWS....
C***           1...  DECLINATION (DEG.)
C***           2...  EQUATION OF TIME ADJUSTMENT (HRS.)
C***           3...  TRUE SOLAR TIME (HRS.)
C***           4...  HOUR ANGLE (DEG.)
C***           5...  SOLAR ELEVATION (DEG.)
C***           6...  OPTICAL AIRMASS
C***     0 < NV < 7.  OTHERWISE, D = 9999.
C***
      DIMENSION MD(11)
      DATA MD/31,29,31,30,31,30,2*31,30,31,30/
      DATA A,B,C,SIGA/0.15,3.885,1.253,279.9348/
      RAD=572957.75913E-4
      SDEC=39784.988432E-5
      RE=1.
      IF(SLO.LT.0.) RE=-1.
      KZ=TZ
      TC=(TZ-KZ)*RE
      TZZ=KZ*RE
      SLB=SLA/RAD
      K=ID
      TIMH=TIME/100.
      I=TIMH
      TIMLOC=(TIMH-I)/0.6+I+TC
      IMC=IM-1
      IF(IMC.LT.1) GOTO2
      DO1I=1,IMC
    1 K=K+MD(I)
    2 LEAP=1
      NL=MOD(IY,4)
      IF(NL.LT.1) LEAP=2
      SMER=TZZ*15.
      TK=((SMER-SLO)*4.)/60.
      KR=1
      IF(K.GE.61.AND.LEAP.LT.2) KR=2
      DAD=(TIMLOC+TZZ)/24.
      DAD=DAD+K-KR
      DF=DAD*360./365.242
      DE=DF/RAD
      DESIN=SIN(DE)
      DECOS=COS(DE)
      DESIN2=SIN(DE*2.)
```

```
      DECOS2=COS(DE*2.)
      SIG=SIGA+DF+1.914827*DESIN-0.079525*DECOS+0.019938*DESIN2-0.00162*
     $DECOS2
      SIG=SIG/RAD
      DECSIN=SDEC*SIN(SIG)
      EFFDEC=ASIN(DECSIN)
      IF(NV.NE.1) GOTO10
      D=EFFDEC*RAD
      RETURN
   10 EQT=0.12357*DESIN-0.004289*DECOS+0.153809*DESIN2+0.060783*DECOS2
      IF(NV.NE.2) GOTO11
      D=EQT
      RETURN
   11 TST=TK+TIMLOC-EQT
      IF(NV.NE.3) GOTO12
      D=TST
      IF(D.LT.0.) D=D+24.
      IF(D.GE.24.) D=D-24.
      RETURN
   12 HRANGL=ABS(TST-12.)*15.
      IF(NV.NE.4) GOTO13
      D=HRANGL
      RETURN
   13 HRANGL=HRANGL/RAD
      SOLSIN=DECSIN*SIN(SLB)+COS(EFFDEC)*COS(SLB)*COS(HRANGL)
      SOLEL= ASIN(SOLSIN)*RAD
      IF(NV.NE.5) GOTO14
      D=SOLEL
      RETURN
   14 IF(NV.NE.6) GOTO8
      IF(SOLEL.LE.0.) GOTO8
      TK=SOLEL+B
      E=1./TK**C
      D=1./(A*E+SOLSIN)
      RETURN
    8 D=9999.
      RETURN
      END
>
```

```
*RATECONSTANT.SPLNA
              SUBROUTINE SPLNA (N,X,Y,J,D,C,W)
              DIMENSION X(10),Y(10),D(2),C(30),W(30)
      C       ------------------------------------------------------------
      C               OVER THE INTERVAL X(I) TO X(I+1), THE INTERPOLATING
      C               POLYNOMIAL
      C                    Y=Y(I)+A(I)*Z+B(I)*Z**2+E(I)*Z**3
      C               WHERE Z=(X-X(I))/(X(I+1)-X(I))
      C               IS USED. THE COEFFICIENTS A(I),B(I) AND E(I) ARE COMPUTED
      C               BY SPLNA AND STORED IN LOCATIONS C(3*I-2),C(3*I-1) AND
      C               C(3*I) RESPECTIVELY.
      C               WHILE WORKING IN THE ITH INTERVAL,THE VARIABLE Q WILL
      C               REPRESENT Q=X(I+1) - X(I), AND Y(I) WILL REPRESENT
      C               Y(I+1)-Y(I)
      C       ------------------------------------------------------------
      C
              Q=X(2) - X(1)
              YI =Y(2) - Y(1)
              IF (J.EQ.2) GO TO 100
      C       ------------------------------------------------------------
      C               IF THE FIRST DERIVATIVE AT THE END POINTS IS GIVEN,
      C               A(1) IS KNOWN, AND THE SECOND EQUATION BECOMES
      C               MERELY B(1)+E(1)=YI - Q*D(1).
      C       ------------------------------------------------------------
              C(1)=Q*D(1)
              C(2)=1.0
              W(2)=YI-C(1)
              GO TO 200
      C       ------------------------------------------------------------
      C               IF THE SECOND DERIVATIVE AT THE END POINTS IS GIVEN
      C               B(1) IS KNOWN, THE SECOND EQUATION BECOMES
      C               A(1)+E(1)=YI-0.5*Q*Q*D(1). DURING THE SOLUTION OF
      C               THE 3N-4 EQUATIONS,A1 WILL BE KEPT IN CELL C(2)
      C               INSTEAD OF C(1) TO RETAIN THE TRIDIAGONAL FORM OF THE
      C               COEFFICIENT MATRIX.
      C       ------------------------------------------------------------
      100     C(2)=0.0
              W(2)=0.5*Q*Q*D(1)
      200     M=N-2
              IF(M.LE.0) GO TO 350
      C       ------------------------------------------------------------
      C               UPPER TRIANGULARIZATION OF THE TRIDIAGONAL SYSTEM OF
      C               EQUATIONS FOR THE COEFFICIENT MATRIX FOLLOWS--
      C       ------------------------------------------------------------
              DO 300 I=1,M
              AI=Q
              Q=X(I+2)- X(I+1)
              H=AI/Q
              C(3*I)=-H/(2.0-C(3*I-1))
              W(3*I)=(-YI-W(3*I-1))/(2.0 - C(3*I-1))
              C(3*I+1)=-H*H/(H-C(3*I))
              W(3*I+1)=(YI-W(3*I))/(H-C(3*I))
              YI=Y(I+2)- Y(I+1)
              C(3*I+2)=1.0/(1.0-C(3*I+1))
      300     W(3*I+2)=(YI-W(3*I+1))/(1.0-C(3*I+1))
      C       ------------------------------------------------------------
```

```
C              E(N-1) IS DETERMINED DIRECTLY FROM THE LAST EQUATION
C              OBTAINED ABOVE, AND THE FIRST OR SECOND DERIVATIVE
C              VALUE GIVEN AT THE END POINT.
C       -----------------------------------------------------------------
350     IF(J.EQ.1) GO TO 400
        C(3*N-3)=(Q*Q*D(2)/2.0-W(3*N-4))/(3.0- C(3*N-4))
        GO TO 500
400     C(3*N-3)=(Q*D(2)-YI-W(3*N-4))/(2.0-C(3*N-4))
500     M=3*N-6
        IF(M.LE.0) GO TO 700
C       -----------------------------------------------------------------
C              BACK SOLUTION FOR ALL COEFFICENTS EXCEPT
C              A(1) AND B(1) FOLLOWS--
C       -----------------------------------------------------------------
        DO 600 II=1,M
        I=M-II+3
600     C(I)=W(I)-C(I)*C(I+1)
700     IF(J.EQ.1) GO TO 800
C       -----------------------------------------------------------------
C              IF THE SECOND DERIVATIVE IS GIVEN AT THE END POINTS,
C              A(1) CAN NOW BE COMPUTED FROM THE KNOWN VALUES OF
C              B(1) AND E(1). THEN A(1) AND B(1) ARE PUT INTO THEIR
C              PROPER PLACES IN THE C ARRAY.
C       -----------------------------------------------------------------
        C(1)=Y(2) - Y(1)-W(2)-C(3)
        C(2)=W(2)
        RETURN
800     C(2)=W(2)-C(3)
        RETURN
        END
>
```

```
*RATECONSTANT.SPLNB
          SUBROUTINE SPLNB (N,X,Y,C,V)
          DIMENSION X(10),Y(10),C(30),V(5)
          V(5)=2.0
          LIM=N-1
C                   -----------------------------------------------------
C                   DETERMINE IN WHICH INTERVAL THE INDEPENDENT
C                   VARIABLE,V(1),LIES.
C                   -----------------------------------------------------
          DO 10 I=2,LIM
   10     IF(V(1).LT.X(I)) GO TO 20
          I=N
          IF(V(1).GT.X(N)) V(5)=3.0
          GO TO 30
   20     IF(V(1).LT.X(1)) V(5) =1.0
C                   -----------------------------------------------------
C                   Q IS THE SIZE OF THE INTERVAL CONTAINING V(1).
C                   -----------------------------------------------------
C                   Z IS A LINEAR TRANSFORMATION OF THE INTERVAL
C                   ONTO (0,1) AND IS THE VARIABLE FOR WHICH
C                   THE COEFFICIENTS WERE COMPUTED BY SPLNA.
C                   -----------------------------------------------------
       30 Q=X(I)-X(I-1)
          Z=(V(1)-X(I-1))/Q
          V(2)=((Z*C(3*I-3)+C(3*I-4))*Z+C(3*I-5))*Z+Y(I-1)
          V(3)=((3.*Z*C(3*I-3)+2.0*C(3*I-4))*Z+C(3*I-5))/Q
          V(4)=(6.*Z*C(3*I-3)+2.0*C(3*I-4))/(Q*Q)
          RETURN
          END
>
```

```
*RATECONSTANT.CLOCK
          REAL FUNCTION CLOCK(T1,IINC)
C
C    ****     ADD A TIME IN MINUTES TO A 2400 HOUR TIME AND RETURN A 2400
C    ****     HOUR TIME
C
          T2 = IINC
          I100 = T1/100
          T3 = T1-100.0*I100 + T2
          I100 = I100 + INT(T3/60)
          CLOCK=I100*100.0 + T3 -60.0 * INT(T3/60)
          RETURN
          END
```

APPENDIX B

LISTING OF SAMPLE DATA SET

An example of a data set for the photolytic rate constant program is listed below. Information is contained therein for the computation of photolytic rate constants for eleven species at Los Angeles, California, on June 21, 1975, from 0400 to 2100 hours. Each line of the following data set represents a single data card. The exact format for all input data to the program is specified in Appendix C, the User's Guide. However, a brief explanation of the sample data set is included here.

Line No.	Comments
1	Location for which photolytic rate constants are to be computed: name of location, latitude, and longitude.
2	Time zone and date (year, month, day).
3	Time range and increment for which rate constants are to be computed.
4	No. of species, no. of zenith angles, no. of wavelength intervals, center point of initial wavelength interval, and wavelength increment.
5	Zenith angles used in initial calculation of rate constants (Subroutine: RATE).
6-109	Values of actinic irradiance, $J(\lambda,\theta)$, for all wavelength intervals λ, and zenith angles θ.
110-154	Species information including wavelength band of absorption, absorption cross sections $\sigma(\lambda)$, and primary quantum yields $\phi(\lambda)$ for each photolytic species.

```
  LOS ANGELES, CALIF.            34.058    118.250
  8.0    1975     6     21
0400    2100       15
  11  10  522900 100
  0. 10. 20. 30. 40. 50. 60. 70. 78. 86.
  .0001500  .0001500  .0000000  .0000000  .0000000  .0000000  .0000000  .0000000
  .0000000  .0000000
  .0398350  .0380150  .0325460  .0246470  .0155188  .0074586  .0022850  .0003046
  .0000000  .0000000
  .4394000  .4813000  .4012000  .3505500  .2814000  .1978000  .1104300  .0392490
  .0092690  .0009416
  .9551000  .9438000  .9006000  .8261000  .7174000  .5706000  .3890000  .1937200
  .0637200  .0088930
 1.6132000 1.5944000 1.5384000 1.4402000 1.2922000 1.0832000  .8031000  .4628000
  .2029100  .0389400
 1.7134000 1.6964000 1.6450000 1.5547000 1.4160000 1.2153000  .9357000  .5726000
  .2689000  .0614900
 1.8924000 1.8748000 1.8237000 1.7327000 1.5915000 1.3834000 1.2429000  .6841000
  .3276000  .0765300
 1.9508000 1.9335000 1.8849000 1.7982000 1.6621000 1.4590000 1.1638000  .7493000
  .3626000  .0834100
 2.3974000 2.3782000 2.3233000 2.2238000 2.0668000 1.8310000 1.4799000  .9722000
  .4767000  .1065300
 2.3177000 2.3008000 2.2508000 2.1609000 2.0189000 1.8026000 1.4751000  .9879000
  .4913000  .1065000
 2.3415000 2.3254000 2.2789000 2.1947000 2.0594000 1.8520000 1.5336000 1.0468000
  .5291000  .1113600
 3.1737000 3.1530000 3.0929000 2.9841000 2.8100000 2.5412000 2.1246000 1.4744000
  .7580000  .1555700
 3.9935000 3.9685000 3.8957000 3.7652000 3.5559000 3.2319000 2.7246000 1.9188000
 1.0035000  .2017300
 4.1188000 4.0949000 4.0250000 3.8985000 3.6956000 3.3780000 2.8754000 2.0589000
 1.0973000  .2153800
 4.2224500 4.1180000 4.0509500 3.9301500 3.7348000 3.4279500 2.9379000 2.1285500
 1.1513500  .2226250
 4.6172000 4.5120000 4.4421000 4.3168499 4.1135000 3.7932000 3.2742000 2.4022500
 1.3207000  .2506650
 5.2089000 5.1817000 5.1007500 4.9576500 4.7279500 4.3661000 3.7832500 2.7996500
 1.5589500  .2921350
 5.6146000 5.5851500 5.4983500 5.3444500 5.0991000 4.7150000 4.0991000 3.0552500
 1.7205500  .3188350
 5.7505000 5.7211000 5.6363000 5.4851000 5.2420000 4.8484500 4.2483000 3.1934500
 1.8205500  .3330000
 5.7988000 5.7708000 5.6876500 5.5407500 5.3036000 4.9180000 4.3271000 3.2775000
 1.8874500  .3398000
 5.7835500 5.7564500 5.6759000 5.5333000 5.3046500 4.9435500 4.3521500 3.3168000
 1.9265000  .3416000
 5.8866000 5.8571500 5.7735000 5.6254000 5.3897000 5.0215500 4.4222500 3.3773000
 1.9704500  .3420500
 5.9349500 5.9050500 5.8182500 5.6660000 5.4247000 5.0527000 4.4501500 3.4050000
 1.9941500  .3394000
 5.9323000 5.9032000 5.8178500 5.6686000 5.4327000 5.0667000 4.4724000 3.4337500
 2.0198000  .3376000
 5.9797000 5.9503500 5.8656000 5.7171000 5.4816500 5.1156000 4.5209500 3.4756000
 2.0455000  .3312500
```

```
5.9271500 5.8988000 5.8161500 5.6701500 5.4392500 5.0801500 4.4947500 3.4615500
2.0399500  .3217000
5.9095500 5.8814500 5.7972500 5.6504500 5.4197000 5.0612000 4.4787000 3.4521000
2.0371500  .3147000
5.9687500 5.9396500 5.8528500 5.7025500 5.4671000 5.1035000 4.5142000 3.4785500
2.0515500  .3088500
6.0576000 6.0280000 5.9412000 5.7889500 5.5507000 5.1827500 4.5850500 3.5335500
2.0813000  .3034500
6.1739000 6.1445000 6.0576000 5.9047000 5.6665000 5.2964000 4.7142000 3.6287000
2.1482000  .3108000
6.2265000 6.1975000 6.1110000 5.9585000 5.7225000 5.3540000 4.7538500 3.6857000
2.1941000  .3201000
6.2692500 6.2397500 6.1517500 5.9972500 5.7577500 5.3875000 4.7846750 3.7140000
2.2183000  .3236750
6.3120000 6.2820000 6.1925000 6.0360000 5.7930000 5.4210000 4.8155000 3.7423000
2.2425000  .3272500
6.3210000 6.2917500 6.2047500 5.9370000 5.6377500 5.4517500 4.8578000 3.7983500
2.3026500  .3494500
6.3300000 6.3015000 6.2170000 5.8380000 5.4825000 5.4825000 4.9001000 3.8544000
2.3628000  .3716500
6.4215000 6.3922500 6.3060000 6.0392500 5.7432500 5.5620000 4.9790500 3.9345500
2.4376250  .4003750
6.5130000 6.4830000 6.3950000 6.2405000 6.0040000 5.6415000 5.0580000 4.0147000
2.5124500  .4291000
6.5937500 6.5630000 6.4720000 6.3142500 6.0740000 5.7082500 5.1225000 4.0785750
2.5737000  .4548250
6.6745000 6.6430000 6.5490000 6.3880000 6.1440000 5.7750000 5.1870000 4.1424500
2.6349500  .4805500
6.6590000 6.6265000 6.5367500 6.3787500 6.1392500 5.7772500 5.1992500 4.1676250
2.6706250  .4994500
6.6435000 6.6100000 6.5245000 6.3695000 6.1345000 5.7795000 5.2115000 4.1928000
2.7063000  .5184000
6.46      6.45      6.35      6.20      5.98      5.71      5.15      4.09
2.74      0.53
6.40      6.38      6.29      6.14      5.91      5.65      5.11      4.07
2.75      0.54
6.34      6.32      6.22      6.08      5.87      5.60      5.05      4.05
2.76      0.56
6.27      6.25      6.16      6.02      5.80      5.55      5.02      4.04
2.77      0.56
6.21      6.19      6.10      5.96      5.75      5.49      4.97      4.02
2.78      0.58
6.14      6.12      6.03      5.90      5.68      5.43      4.92      4.00
2.79      0.59
6.08      6.06      5.97      5.84      5.64      5.40      4.90      3.99
2.79      0.59
6.02      6.00      5.91      5.78      5.58      5.34      4.86      3.97
2.79      0.59
5.95      5.94      5.85      5.72      5.53      5.31      4.84      3.96
2.79      0.60
5.89      5.88      5.79      5.66      5.47      5.25      4.80      3.94
2.78      0.60
5.82      5.81      5.73      5.59      5.42      5.22      4.78      3.93
2.78      0.60
1   NO2  2900  4500
0.99E-191.41E-192.18E-192.98E-193.74E-194.54E-195.20E-195.69E-196.04E-196.23E-19
6.38E-196.53E-196.38E-196.23E-195.88E-195.54E-195.20E-19
```

```
    0.988     0.980     0.972     0.964     0.956     0.948     0.940     0.932     0.924     0.916
    0.908     0.699     0.175     0.025     0.006     0.001     0.000
  2  HONO   3000   3900
0.79E-201.14E-201.75E-202.86E-204.23E-205.29E-203.98E-206.08E-203.33E-201.78E-20
00000000
   1.00      1.00      1.00      1.00      1.00      1.00      1.00      1.00      1.00      0.00
00000000
  3  HNO3   2900   3200
6.34E-212.76E-219.50E-221.80E-22
   1.00      1.00      1.00      0.00
  4  O33P   2900   7500
1.62E-184.44E-191.19E-193.36E-208.79E-211.94E-213.86E-22
                                                              1.99E-223.60E-225.38E-227.48E-22
9.58E-221.31E-211.74E-212.20E-212.76E-213.31E-213.78E-214.54E-215.09E-214.93E-21
5.15E-215.52E-214.98E-214.17E-213.61E-213.18E-212.69E-212.17E-211.79E-211.52E-21
1.26E-219.77E-228.06E-226.76E-225.56E-224.84E-224.07E-22
    0.0       0.0       1.0       1.0       1.0       1.0       1.0       0.0       0.0       0.0
    0.0       0.0       0.0       0.0       0.0       0.0       1.0       1.0       1.0       1.0
    1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0
    1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0
    1.0       1.0       1.0       1.0       1.0       1.0       1.0
  5  O31D   2900   3100
1.62E-184.44E-191.19E-193.36E-208.79E-211.94E-213.86E-22
    1.0       1.0       1.0
  6  O3SD   2900   3500
1.62E-184.44E-191.19E-193.36E-208.79E-211.94E-213.86E-22
    1.0       1.0       1.0       1.0       1.0       1.0       1.0
  7  FOR1   2900   3600
3.18E-203.25E-203.15E-202.34E-202.37E-201.98E-208.37E-211.76E-21
    0.81      0.66      0.52      0.40      0.29      0.18      0.09      0.01
  8  FOR2   2900   3600
3.18E-203.25E-203.15E-202.34E-202.37E-201.98E-208.37E-211.76E-21
    0.19      0.34      0.48      0.60      0.71      0.82      0.91      0.99
  9  H2O2   2900   3700
1.49E-209.94E-216.88E-214.97E-213.82E-213.01E-211.91E-211.15E-210.76E-21
    1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0       1.0
 10  ACA1   2900   3400
4.66E-204.09E-202.96E-201.69E-206.92E-211.34E-21
    0.329     0.274     0.221     0.158     0.100     0.041
 11  ACA2   2900   3100
4.66E-204.09E-202.96E-201.69E-206.92E-211.34E-21
    0.087     0.036     0.007
```

APPENDIX C
USER'S GUIDE

The photolytic rate constant program may easily be run with the sample data set provided. Should the user wish to change the location, date or time for which the program is run, these inputs are contained on the first three data cards and may easily be amended to fit the needs of the user. The following User's Guide describes the format of these first three data cards, as well as the rest of the cards should more extensive changes be desired.

Further, a listing of all photolytic reactions currently handled by the rate constant program is provided. The alphameric representation of each species as used in the program is listed.

SPECIES INFORMATION INCLUDED ON CARDS PROVIDED FOR USER

SPECIES NO. / SPECIES NAME	ALPHAMERIC REPRESENTATION	REACTION (A + hν $\xrightarrow{\text{MINLAM (Å)} \leq \lambda \leq \text{MAXLAM (Å)}}$ B)
1 NITROGEN DIOXIDE	NO2	$NO_2 + h\nu \xrightarrow{2900 \leq \lambda \leq 4500} NO + O(^3P)$
2 NITROUS ACID	HONO	$HONO + h\nu \xrightarrow{3000 \leq \lambda \leq 3900} HO + NO$
3 NITRIC ACID	HNO3	$HONO_2 + h\nu \xrightarrow{2900 \leq \lambda \leq 3200} HO + NO_2$
4 OZONE	O33P	$O_3 + h\nu \xrightarrow{2900 \leq \lambda \leq 7500} O(^3P) + O_2$
5 OZONE	O31D	$O_3 + h\nu \xrightarrow{2900 \leq \lambda \leq 3100} O(^1D) + O_2$
6 OZONE	O3SD	$O_3 + h\nu \xrightarrow{2900 \leq \lambda \leq 3500} O_2\ (^1\Delta) + O$
7 FORMALDEHYDE	FOR1	$H_2CO + h\nu \xrightarrow{2900 \leq \lambda \leq 3600} H + HCO$
8 FORMALDEHYDE	FOR2	$H_2CO + h\nu \xrightarrow{2900 \leq \lambda \leq 3600} H_2 + CO$
9 HYDROGEN PEROXIDE	H2O2	$H_2O_2 + h\nu \xrightarrow{2900 \leq \lambda \leq 3700} 2HO$
10 ACETALDEHYDE	ACA1	$CH_3CHO + h\nu \xrightarrow{2900 \leq \lambda \leq 3400} CH_3 + HCO$
11 ACETALDEHYDE	ACA2	$CH_3CHO + h\nu \xrightarrow{2900 \leq \lambda \leq 3100} CH_4 + CO$

DATA INPUT TO RATE CONSTANT PROGRAM

Card No.	Column No.	Variable	Format	Units	Comments
1	1-24	PLACE	6A4	-	This is the alphameric name of the location for which the rate constant computations are to be made.
1	30-39	SLA	F10.4	DEGREES +=North Lat. -=South Lat.	Latitude of PLACE
1	40-49	SLO	F10.4	DEGREES +=West Long. -=East Long.	Longitude of PLACE
2	1-5	TZ	F5.1	-	Number of time zones distant from Greenwich Mean Time (G.M.T.), i.e. L.A. DEN. CHI. N.Y. LONDON PARIS ATHENS ....(G.M.T.) 8. 7. 6. 5. 0. 1. 2. etc. also includes fraction if local time is not standard meridian time: eg. Poona, India = 5.5
2	10-13	IY	I4	-	Year for which computations are to be made
2	18-19	IM	I2	-	Month
2	24-25	ID	I2		Day
3	1-4	JSTRT	I4	Time (24-Hr Clock)	Time of day to begin listing of photolytic rate constants (Local Standard Time)

Card No.	Column No.	Variable	Format	Units	Comments
3	9-12	JSTOP	I4	Time (24-Hr Clock)	Time of day to end listing of photolytic rate constants (Local Standard Time)
3	19-20	IINC	I2	Minutes	Time increment to use in listing of rate constants (IINC ≥ 1 minute).

NOTE: The previous three cards must be supplied by the user for proper execution of the program. All subsequent data input cards have been supplied for the user, along with the program deck. Should the user wish to make changes of his own, these cards are described below.

Card No.	Column No.	Variable	Format	Units	Comments
4	1-4	MAXL	I4	-	Number of species for which rate constants are to be computed.
4	5-8	MAXZ	I4	-	Number of zenith angles used for base values with inputs of J, the actinic irradiance.
4	9-12	MAXJ	I4	-	The number of wavelength values for which corresponding values of J are input.
4	13-16	LAM1	I4	Å	Initial wavelength value for which values of J are input.
4	17-20	INC	I4	Å	Constant increment value for updating wavelength. (This is also the size of the wavelength interval over which the values of J have been averaged.)

Card No.	Column No.	Variable	Format	Units	Comments
5	1-80	Z	20F4.0	Degrees	Values of zenith angles used with inputs of J. The number of angles must equal MAXZ.
6-109	1-80	J	8F10.7,/, 2F10.7	$\frac{\text{Photons} \times 10^{15}}{\text{cm}^2\text{-sec-Å interval}}$	Each card lists MAXZ values of J, the actinic irradiance, corresponding to the values of Z input on card no. 5. There are MAXZ cards of this form; the first of which corresponds to the J values at LAM1, next at LAM1 + INC, LAM1 + 2·INC, etc.

NOTE: A complete set of the following three types of cards is needed for each species included in the rate constant computations.

Card No.	Column No.	Variable	Format	Units	Comments
110	1-2	L	I2	-	Species number ($1 \leq L \leq$ MAXL)
110	5-8	SPECIE	A4	-	Alphameric designation of species L.
110	11-14	MINLAM	I4	Å	Starting wavelength in rate constant computations for species L.
110	17-20	MAXLAM	I4	Å	Ending wavelength in rate constant computations for species L.

Card No.	Column No.	Variable	Format	Units	Comments
111-112	1-80	SIGMA	(10E8.2,/)	CM^2	Values of absorption cross-sections for species L, at wavelengths from MINLAM to MAXLAM in increments of INC.
113-114	1-80	PHI	(10F8.4,/)	-	Values of primary quantum yields for species L, at wavelengths from MINLAM to MAXLAM in increments of INC.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/4-77-015	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE CALCULATION OF SELECTED PHOTOLYTIC RATE CONSTANTS OVER A DIURNAL RANGE A Computer Algorithm		5. REPORT DATE March 1977 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) Kenneth L. Schere and Kenneth L. Demerjian		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Sciences Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, N.C. 27711		10. PROGRAM ELEMENT NO. 1AA603 11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Sciences Research Laboratory - RTP, NC, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, N.C. 27711		13. TYPE OF REPORT AND PERIOD COVERED In-House 14. SPONSORING AGENCY CODE EPA/600/09

15. SUPPLEMENTARY NOTES

16. ABSTRACT A computer program has been created and is described herein which employs the theoretical formulation of the photolytic rate constant to calculate these rate constants for specific chemical species over a diurnal time period in clear-sky conditions. A user of the program must specify the date, time and location for which the rate constants are desired. With this information and specific data on zenith angles, solar irradiance, and species characteristics of absorption cross-sections and primary quantum yields, which are provided in the program package, the computer program generates a diurnal range of photolytic rate constants for each species. The species included are NO_2, O_3, HONO, $HONO_2$, H_2CO, CH_3CHO, and H_2O_2. The appendices to this report contain program and data listings as well as a User's Guide to program operation.

The program-generated photolytic rate constants for NO_2 are compared to direct measurements of this quantity as taken at Research Triangle Park, N.C. during April 1975. The two methods are generally in close agreement after the theoretically computed rate constants are scaled by a simplistic method for the compensation of solar radiation attention by clouds.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
*Air Pollution *Photochemical Reactions *Reaction Kinetics *Atmospheric Modeling *Computerized Simulation *Computer Programs *Algorithms		13B 07E 07D 14A 14B 09B 12A

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