# NATIONAL BUREAU OF STANDARDS REPORT

NBS 9518

Quarterly Report

AIR POLLUTION PROGRAM

NATIONAL BUREAU OF STANDARDS

January 1, 1967 to March 31, 1967

by

A. Cohen

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Division of Analytical Chemistry

Division of Metrology

and

Division of Physical Chemistry

Report of Air Pollution Project

Sponsored by U. S. Public Health Service

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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**NBS PROJECT**

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## ORGANIC CHEMISTRY

### 1. Detection of Impurities in, and Purification of, Commercial Compounds

a. Fluorene.- The impurities in a sample of commercial fluorene ("white label" grade) were detected by thin-layer chromatography. A sample (about 2 μg) of the fluorene was spotted on a glass plate bearing silica gel G (250-μm layer, 5 X 20 cm) which was then placed in a chamber and developed with 1:1 (v/v) heptane—benzene; developing time, 60 min. The plate was then dried in a hood, sprayed with a 10% solution of concentrated sulfuric acid in methanol, and heated at 100° for 3 min. The following spots were observed: (1) colorless to very pale blue (blue fluorescence), $\underline{R}_F$ 0.86 ± 0.01, fluorene; (2) deep blue-purple (not fluorescent), $\underline{R}_F$ 0.37 ± 0.02, carbazole (approximate concentration, 0.5 to 0.75%); (3) colorless, pale bluish green fluorescence, $\underline{R}_F$ 0.00 ± 0.02, unknown.

The commercial fluorene was then purified by column chromatography on a column of florisil (100-200 mesh). A solution of fluorene in benzene (reagent grade) was added to the column, and elution was conducted with 1:1 (v/v) heptane—benzene. The fractions exhibiting a blue fluorescence were collected, combined, and evaporated to dryness, and the crystalline product was recrystallized from absolute ethanol. The pure fluorene was colorless, had mp 116-117°, and showed only one spot (blue fluorescence) on a thin-layer chromatogram.

b. Fluoren-9-one.- Commercial fluoren-9-one ("white label" grade) was examined by thin-layer chromatography, and found to be contaminated with a small proportion of fluorene. The commercial fluoren-9-one was then purified by chromatography on a column of silica gel, with 1:1 (v/v) ethyl acetate—benzene as the eluant. The fractions having a yellow color were collected, combined, and evaporated to dryness, and the crystalline product was recrystallized from absolute ethanol. The pure compound was obtained as yellow crystals, mp 85-86°, and showed only one (yellow) spot on a thin-layer chromatogram.

<u>c. Carbazole.</u>- Commercial carbazole ("white label" grade) was examined by thin-layer chromatography on silica gel G, with 1:1 (v/v) ethyl acetate—benzene as developer, and found (10% methanolic sulfuric acid spray) to contain a contaminant as shown by a blue spot faster than that of carbazole.

## 2. Photochemistry of Aromatic, Air Pollutants

<u>a. Fluorene Adsorbed on Garden Soil.</u>- A solution of purified fluorene (300 mg) in absolute ethanol (10 ml) was mixed with 6 g of purified garden soil; the resulting slurry was spread on a glass plate (20 X 20 cm), dried, and irradiated with ultraviolet light (366 nm) for 200 hr. The mixture was then extracted with acetone, and the extract was examined by thin-layer chromatography on silica gel G (250-μm layer, 5 X 20 cm) on a glass plate, by use of two developers: 18:1:1 (v/v) benzene—*N,N*-dimethylformamide—glacial acetic acid (solvent A), and 8:1:1 (v/v) heptane—glacial acetic acid—ethyl acetate (solvent B).

The following spots were observed. (1)(a) With solvent A (75 min): colorless; blue fluorescence; $R_F$ 0.95 ± 0.01; unreacted fluorene; (b) with solvent B (60 min): colorless; blue fluorescence; $R_F$ 0.73 ± 0.01; unreacted fluorene. (2) Yellow; pink fluorescence; $R_F$ 0.84 ± 0.03 (solvent A), 0.47 ± 0.02 (solvent B); fluoren-9-one. On spraying the chromatogram with 10% methanolic sulfuric acid and heating it for 3 min at 100°, the pink fluorescence of the spot changes to a deep yellow fluorescence; this is characteristic of fluoren-9-one. (3) Colorless; light-blue fluorescence; $R_F$ 0.63 ± 0.02 (solvent A), 0.33 ± 0.03 (solvent B); unknown. (4) Colorless; pinkish fluorescence; $R_F$ 0.59 ± 0.02 (solvent A), 0.25 ± 0.02 (solvent B); unknown. (5) Orange-brown; faint pinkish fluorescence; $R_F$ 0.55 ± 0.01 (solvent A); tentatively identified as 1,2-bis(2,2'-biphenylylene)ethylene. (6) Colorless; greenish blue fluorescence; $R_F$ 0.51 ± 0.02 (solvent A), 0.11 ± 0.01 (solvent B); unknown.

The material comprising spot 2 (yellow) was found to be identical, by ultraviolet and visible spectroscopy, with an authentic sample of pure fluoren-9-one.

b. 1,4-Dihydroxyanthraquinone on Silica Gel.- 1,4-Dihydroxyanthraquinone was applied as spots to plates of activated silica gel G, and to Eastman Chromagram sheets (silica gel). These were then irradiated with a high-intensity ultraviolet lamp (366 nm) for 4 hr. Then, the quinone was applied as the reference compound, and the plates and sheets were developed twice with benzene. Examination under ultraviolet light, and after spraying and charring with methanolic sulfuric acid, revealed no new spots. Consequently, the quinone does not undergo photo-oxidation on silica gel in 4 hr.

c. Attempts to Determine *ortho*-Quinones.- It has been shown that photo-oxidation of anthracene gives anthraquinone and hydroxylated derivatives thereof, but it has not been conclusively demonstrated that an *ortho*-quinone is not formed. The *o*-quinones and their homologs may be detected by sintering with guanidine carbonate, to give a blue-violet color, [1] and preliminary work has now been done in applying this test in thin-layer chromatography. The following compounds were spotted on thin-layer plates of silica gel G: (1) 1,4-naphthoquinone, (2) 1,2-naphthoquinone, (3) anthraquinone, (4) acenaphthenequinone, (5) 1,8-pyrenedione, (6) 1,6-pyrenedione, (7) *p*-benzoquinone, (8) benz[*a*]anthracene-7,12-dione, (9) phenanthrenequinone, and (10) 1,4-dihydroxyanthraquinone. The plates were sprayed with 20% aqueous guanidine carbonate, and heated at 120° for 5 min. Compounds 2, 4, and 9, which are *o*-quinones, might have been expected to show some similarity, either under visible or ultraviolet light; however, this was not found. Under the conditions tried, compound 2 gave a reddish brown spot (visible) that was blue under u. v.; compound 4 gave a faint yellow spot (visible) that was bluish white under u. v.; and compound 9 gave an orange spot (visible) that was not seen under u. v. The other compounds gave spots of the following colors: (visible) 1, reddish brown; 3, pink; 5, reddish brown; 6, brown; 7, brown with a green circumference; 8, yellow; and 10, violet; (ultraviolet) 1, blue-green; 3, pink; 5, negative; 6, blue; 7, blue-green; 8, negative; and 10, negative.

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[1] F. Feigl, "Spot Tests in Organic Analysis," Elsevier, New York, 1960, p.345.

## SURFACE CHEMISTRY SECTION

There is no doubt that the physical processes in the O atom-condensed olefin system differ markedly from those in the H atom-olefin system, previously well studied. Unlike the H atom case, the O atoms react in the interior of the condensed phase. Atomic oxygen apparently has a high solubility in these films, at least those consisting of three-carbon hydrocarbons. In fact, the reaction rate with propylene at 90°K is quite independent of dilution with propane, even over a 100 to 1 ratio of propane to propylene, Table I. Pure propylene reacts equally as well. Undiluted butene-1 shows very little reaction, but dilution with propane increases the apparent rate to a constant value independent of further dilution after about 1/2 to 1 propane to butene-1 has been reached, Table II. The average rate is independent of the reaction time, Table III. Dilution with butane is interesting in that it completely suppresses the O atom reaction with the olefin. The O atom solubility in a butane matrix at 90°K is apparently vanishingly small. An inverse relationship between the solubility and the crystallinity of the condensed phase may be operative, although further work is required in support.

The measurement of relative rates of O atom addition was attempted by determining the products from the reaction with a mixture of two olefins, propylene and butene-1, in a propane matrix. An unusual effect was found. In a butene-1, propylene mixture in an 8 to 1 ratio, most of the products arose from the propylene. As this mixture was diluted, butene-1 products increased and those of propylene decreased. At high propane dilution, the product ratio approached a constant ratio. The initial interpretation was that the initial O atom attack on an olefin gave a triplet intermediate. This triplet was assumed to be able to undergo a reversible O exchange with other olefin molecules. Finally, the triplet became stabilized by either ring closure to form the expoxide or an H atom migration to form the aldehyde.

This scheme was represented as

$$B + O \xrightarrow{k_1} BO^*$$

$$P + O \xrightarrow{k_2} PO^*$$

$$PO^* + B \xrightleftharpoons[k_4]{k_3} BO^* + P$$

$$PO^* \xrightarrow{k_5} PO$$

$$BO^* \xrightarrow{k_6} BO$$

Where B and P represent butene-1 and propylene, PO and BO the oxygenated products, and asterisked quantities the triplet state. This mechanism was discarded on the following basis: If *cis*-butene-2 were used instead of butene-1, then reaction 4, because of the free rotation in the $BO^*$ molecule about the central C-C bond, would result in the formation of *trans*-butene-2. (*Trans*-butene-2 is the thermodynamically stable form at 90°K, and was produced in good yield in the H atom *cis*-butene-2 reaction.) No *trans*-butene-2 was found in the mixture after an O atom reaction. This effectively eliminates the postulated mechanism. We are now considering in some detail a diffusion mechanism to account for the experimental findings. It is still not established whether the ratio at infinite dilution, where the propylene to butene products are in a ratio of about 1.5, can be entirely ascribed to kinetic rates.

# TABLE I

O($^3$P) + propylene/propane films at 90°K. Rhenium filament temperature = 2200°K. Oxygen pressure = 0.5 mtorr. Reaction time = 5 minutes 55μ moles of propylene were used in all experiments. Condensed film surface area 80 cm$^2$

| Propane | (all quantities in μ moles) | | | | Rate | PO |
|---|---|---|---|---|---|---|
| Propylene | PO | PA | A | | $\frac{\mu \text{ moles}}{\text{minute}}$ | PA |
| 0 | 8.2 | 7.3 | 1.0 | 16.2 | 3.2 | 1.12 |
| 1/2 | 6.8 | 6.5 | 1.1 | 14.4 | 2.9 | 1.05 |
| 1 | 4.9 | 4.1 | 0.9 | 9.9 | 2.0 | 1.20 |
| 2 | 4.9 | 4.3 | 0.9 | 10.1 | 2.0 | 1.14 |
| 4 | 5.8 | 5.2 | 0.9 | 11.9 | 2.4 | 1.12 |
| 8 | 5.6 | 5.4 | 1.5 | 12.5 | 2.5 | 1.05 |
| 16 | 7.1 | 6.7 | 1.2 | 15.0 | 3.0 | 1.06 |
| 128 | 4.9 | 4.7 | 0.8 | 10.4 | 2.1 | 1.04 |
| | | | | | 2.5 ± 0.5 | 1.09 ± 0.05 |

| | |
|---|---|
| PO | Propylene oxide |
| PA | Propionaldehyde |
| A | Acetone |
| p | Sum of $C_3$ oxygenated products |

## TABLE II

O($^3$P) + 1-butene/propane films at 90°K. Rhenium filament temperature = 2200°K. Oxygen pressure = 0.5 mtorr. Reaction time = 5 minutes; 55 μ moles of 1-butene were used in all experiments. Condensed film surface area ≈ 80 cm$^2$

| Propane / 1-butene | (all quantities in μ moles) | | | | |
|---|---|---|---|---|---|
| | BO | BA | $\Sigma_B$ | Rate $\left(\frac{\mu\ \text{moles}}{\text{minute}}\right)$ | BO / BA |
| 0 | 0.5 | 0.4 | 0.9 | 0.2* | 1.20 |
| 1/2 | 4.1 | 3.6 | 7.7 | 1.5 | 1.14 |
| 1 | 4.0 | 3.6 | 7.6 | 1.5 | 1.11 |
| 2 | 3.3 | 2.9 | 6.2 | 1.2 | 1.14 |
| 4 | 3.8 | 3.4 | 7.2 | 1.4 | 1.12 |
| 8 | 4.0 | 3.5 | 7.5 | 1.5 | 1.14 |
| 16 | 3.4 | 3.0 | 6.4 | 1.3 | 1.13 |
| 32 | 3.3 | 2.9 | 6.2 | 1.2 | 1.14 |
| 64 | 2.7 | 2.5 | 5.2 | 1.0 | 1.08 |
| | | | | 1.3 ± 0.2*. | 1.13 ± 0.02 |

BO = 1,2-butene oxide

BA = n-butyraldehyde

$\Sigma_B$ = 1,2 butene oxide + n-butyraldehyde

* Mean value of reaction rate was obtained without including the pure 1-butene film.

## TABLE III

O($^3$P) + $\frac{4}{1}$ ($^{\text{propane}}$/1-butene) film at 90°K. Re filament temperature = 2200°K; oxygen pressure = 0.5 mtorr; film surface area = 80 cm$^2$; and 55 $\mu$ moles of 1-butene used in all experiments.

| Reaction time (minutes) | (all quantities in $\mu$ moles) BO | BA | | Rate $\frac{\mu \text{ moles}}{\text{minute}}$ |
|---|---|---|---|---|
| 1 | 1.0 | 0.9 | 1.9 | 1.9 |
| 2 | 2.0 | 1.7 | 3.7 | 1.9 |
| 3 | 2.4 | 2.1 | 4.5 | 1.5 |
| 4 | 2.7 | 2.2 | 4.9 | 1.2 |
| 5 | 3.8 | 3.4 | 7.2 | 1.4 |
| 10 | 6.3 | 5.2 | 11.5 | 1.2 |
| | | | | 1.5 ± 0.3 |

TABLE IV

O($^3$P) + $\frac{8}{1}$ $\frac{\text{1-butene}}{\text{propylene}}$ films diluted with propane at 90°K. Rhenium filament temperature = 2200°K. Oxygen pressure = 0.5 mtorr. Reaction time = 5 minutes. Condensed film surface area ≈ 80 cm$^2$

| Reactants (μ moles) | | | Products (μ moles) | | | | | | | (μ moles) | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_3H_8$ | $C_3H_6$ | $C_4H_8$ - 1 | PO | PA | A | $\sum_p$ | BO | BA | $\sum_B$ | $\sum_p + \sum_B$ | $\sum_p / \sum_B$ |
| 0 | 55 | 440 | 2.4 | 2.0 | 0.3 | 4.7 | 0.4 | 0.3 | 0.7 | 5.4 | 6.7 |
| 250 | 27 | 220 | 2.2 | 2.0 | 0.4 | 4.6 | 0.8 | 0.7 | 1.5 | 6.1 | 3.1 |
| 660 | 27 | 220 | 1.4 | 1.3 | 0.3 | 3.0 | 1.0 | 0.9 | 1.9 | 4.9 | 1.6 |
| 1100 | 27 | 220 | 1.0 | 1.0 | 0.2 | 2.2 | 1.6 | 1.5 | 3.1 | 5.3 | 0.71 |
| 2200 | 27 | 220 | 0.9 | 0.9 | 0.2 | 2.0 | 2.3 | 2.1 | 4.4 | 6.4 | 0.45 |
| 2475 | 14 | 110 | 0.8 | 0.8 | 0.2 | 1.8 | 3.4 | 2.6 | 6.0 | 7.8 | 0.30 |
| 4950 | 14 | 110 | 0.6 | 0.6 | 0.2 | 1.4 | 3.2 | 2.7 | 5.9 | 7.3 | 0.24 |
| 5500 | 27 | 27 | 3.2 | 2.9 | 0.2 | 6.3 | 2.2 | 1.9 | 4.1 | 7.2 | 1.5 |
| 4950 | 110 | 14 | 2.4 | 2.2 | 0.3 | 4.9 | 0.2 | 0.1 | 0.3 | 5.2 | 16.3 |

## SOLAR RADIATION

The two photoelectric-filter spectroradiometers previously used in the measurement of ultra-violet solar irradiance on a horizontal surface were intercompared at the NBS Gaithersburg outdoor location. The intercomparison consisted of placing the two instrumentations next to each other (each instrument having the same orientation), calibrating each spectroradiometer with the same standard of spectral irradiance, and then measuring the solar irradiance during various intervals throughout the day. A recalibration of both instruments was performed after each measuring interval. The picoammeterswhich measure the current output of the photoelectric detectors were checked for accuracy through the use of a calibrated picoampere current source, and the linearity of the strip chart recorders was determined through the use of both the picoammeter and the picoampere current source. Errors as large as 2 percent were present for various ranges on the picoammeters, and the appropriate corrections were accordingly applied to the final results. No significant errors due to recorder non-linearity were observed. The ultra-violet solar irradiance as determined with each spectroradiometer differed by as much as 3 percent throughout the day, with the average difference between the two set-ups being about 2 percent.

For a relatively clear atmospheric measuring station, one spectroradiometer was set up at the Sterling Research Center, Sterling, Virginia (about 20 miles from Washington, D. C. - elevation 281 ft.), whereas the other instrument was located in downtown Washington (on the roof of a 10-story building at 601 Indiana Ave. N.W.)

The average incoming ultra-violet solar irradiance for 2 days in December (NBS Gaithersburg location only) and for 3 days in March (Sterling and downtown Washington locations) in watt/meter$^2$ - 10-nm wavelength intervals for 30-minute periods throughout the day are shown in Tables 1-9.

## NOTES ON WEATHER AND SMOG

### December 12 - Gaithersburg, Md.

Sky relatively clear until mid-afternoon, when cirrus clouds appeared in the western sky, causing partial obscuration of the sun. Little or no wind, with light reddish brown smog near the horizon throughout the day.

### December 15 - Gaithersburg, Md.

Very similar to Dec. 12, but with moderate northern wind and increased smog near the horizon.

### March 3 - Sterling, Va.

Thin cirrus covering most of the sky in the morning, followed by slight clearing in the afternoon. Continuous light southerly wind all day. Light smog visible near the horizon.

### March 3 - Downtown Wash. D. C.

Light intermittent clouds all day. Moderate to heavy smog in the morning, clearing somewhat in the afternoon.

### March 27 - Sterling, Va.

Light to moderate cloud accumulation before 10 a.m.; completely overcast sky during the remainder of the day.

March 27 - Downtown Wash. D. C.

Very thin cirrus clouds in early morning, followed by increasing cloudiness becoming completely overcast after 12:00. Smog light to moderate.

March 30 - Sterling, Va.

Very clear all day, except for light occasional clouds about 11:00 a.m.

March 30 - Downtown Wash. D. C.

Very clear all day except for scattered cumulus clouds between 10:00 a.m. and 12:30 p.m. resulting from a light southerly wind during this period. Heavy smog throughout the day.

## TABLE 1

## AVERAGE INCOMING 305-315-nm RADIATION (W/M$^2$) FOR 30-MINUTE INTERVALS IN 1966-7

| | DOWNTOWN WASH. D. C. | | | STERLING VIRGINIA | | | GAITHERSBURG MARYLAND | |
|---|---|---|---|---|---|---|---|---|
| TRUE SOLAR TIME | MAR. 3 | MAR. 27 | MAR. 30 | MAR. 3 | MAR. 27 | MAR. 30 | DEC. 12 | DEC. 15 |
| 8:45 | .222 | .390 | .432 | .233 | .355 | .508 | .095 | .093 |
| 9:15 | .318 | .525 | .585 | .407 | .504 | .663 | .176 | .153 |
| 9:45 | .409 | .609 | .726 | .509 | .670 | .827 | .258 | .216 |
| 10:15 | .453 | .701 | .867 | .665 | .646 | .983 | .332 | .288 |
| 10:45 | .621 | .842 | .930 | .774 | .630 | 1.04 | .400 | .353 |
| 11:15 | .729 | .863 | .988 | .834 | .630 | 1.05 | .454 | .396 |
| 11:45 | .755 | .855 | .946 | .837 | .725 | 1.08 | .481 | .417 |
| 12:15 | .738 | .705 | 1.10 | .806 | .709 | 1.11 | .488 | .416 |
| 12:45 | .722 | .634 | 1.07 | .800 | .591 | 1.12 | .468 | .390 |
| 13:15 | .667 | .705 | 1.02 | .749 | .591 | 1.04 | .414 | .347 |
| 13:45 | .586 | .609 | .901 | .661 | .567 | .958 | .346 | .288 |
| 14:15 | .468 | .534 | .772 | .545 | .496 | .860 | .271 | .232 |
| 14:45 | .376 | .421 | .618 | .428 | .331 | .713 | .170 | .155 |
| 15:15 | .290 | .291 | .465 | .315 | .260 | .549 | .095 | .082 |
| 15:45 | .206 | .226 | .334 | .216 | .197 | .369 | .047 | .039 |

### TABLE 2

### AVERAGE INCOMING 315-325-nm RADIATION ($W/M^2$)

### FOR 30-MINUTE INTERVALS IN 1966-7

| TRUE SOLAR TIME | DOWNTOWN WASH. D. C. | | | STERLING VIRGINIA | | | GAITHERSBURG MARYLAND | |
|---|---|---|---|---|---|---|---|---|
| | MAR. 3 | MAR. 27 | MAR. 30 | MAR. 3 | MAR. 27 | MAR. 30 | DEC. 12 | DEC. 15 |
| 8:45 | .703 | 1.08 | 1.17 | .883 | .999 | 1.40 | .378 | .403 |
| 9:15 | .886 | 1.37 | 1.49 | 1.23 | 1.35 | 1.72 | .565 | .545 |
| 9:45 | 1.11 | 1.49 | 1.78 | 1.40 | 1.69 | 2.03 | .752 | .722 |
| 10:15 | 1.23 | 1.66 | 2.06 | 1.73 | 1.59 | 2.31 | .920 | .900 |
| 10:45 | 1.60 | 1.98 | 1.94 | 1.93 | 1.53 | 2.43 | 1.04 | 1.05 |
| 11:15 | 1.81 | 2.00 | 2.27 | 2.07 | 1.50 | 2.43 | 1.18 | 1.14 |
| 11:45 | 1.86 | 1.98 | 1.82 | 2.02 | 1.72 | 2.51 | 1.23 | 1.19 |
| 12:15 | 1.82 | 1.42 | 2.48 | 1.99 | 1.67 | 2.55 | 1.24 | 1.18 |
| 12:45 | 1.78 | 1.47 | 2.45 | 1.96 | 1.40 | 2.59 | 1.20 | 1.12 |
| 13:15 | 1.68 | 1.65 | 2.35 | 1.86 | 1.43 | 2.43 | 1.11 | 1.02 |
| 13:45 | 1.51 | 1.45 | 2.11 | 1.69 | 1.38 | 2.30 | .957 | .878 |
| 14:15 | 1.27 | 1.32 | 1.89 | 1.48 | 1.26 | 2.13 | .794 | .733 |
| 14:45 | 1.09 | 1.08 | 1.58 | 1.21 | .894 | 1.85 | .588 | .541 |
| 15:15 | .995 | .792 | 1.26 | .961 | .755 | 1.50 | .392 | .352 |
| 15:45 | .802 | .662 | .969 | .615 | .616 | 1.12 | .210 | .183 |

## TABLE 3

## AVERAGE INCOMING 325-335 nm RADIATION (W/M$^2$) FOR 30-MINUTE INTERVALS IN 1966-7

| TRUE SOLAR TIME | DOWNTOWN WASH. D. C. | | | STERLING VIRGINIA | | | GAITHERSBURG MARYLAND | |
|---|---|---|---|---|---|---|---|---|
| | MAR. 3 | MAR. 27 | MAR. 30 | MAR. 3 | MAR. 27 | MAR. 30 | DEC. 12 | DEC. 15 |
| 8:45 | 1.29 | 1.88 | 2.01 | 1.52 | 1.63 | 2.24 | .702 | .818 |
| 9:15 | 1.55 | 2.31 | 2.46 | 2.04 | 2.16 | 2.70 | .995 | 1.03 |
| 9:45 | 1.89 | 2.46 | 2.88 | 2.27 | 2.66 | 3.14 | 1.28 | 1.32 |
| 10:15 | 2.08 | 2.72 | 3.35 | 2.75 | 2.46 | 3.53 | 1.54 | 1.60 |
| 10:45 | 2.66 | 3.19 | 3.48 | 3.02 | 2.35 | 3.70 | 1.75 | 1.84 |
| 11:15 | 3.00 | 3.21 | 3.59 | 3.25 | 2.29 | 3.67 | 1.92 | 1.98 |
| 11:45 | 3.02 | 3.15 | 3.21 | 3.14 | 2.63 | 3.80 | 2.01 | 2.05 |
| 12:15 | 2.98 | 2.18 | 3.93 | 3.08 | 2.54 | 3.86 | 2.02 | 2.03 |
| 12:45 | 2.92 | 2.35 | 3.91 | 3.06 | 2.14 | 3.92 | 1.96 | 1.94 |
| 13:15 | 2.78 | 2.64 | 3.75 | 2.92 | 2.20 | 3.71 | 1.82 | 1.78 |
| 13:45 | 2.53 | 2.34 | 3.46 | 2.67 | 2.14 | 3.52 | 1.60 | 1.55 |
| 14:15 | 2.15 | 2.18 | 3.09 | 2.37 | 1.98 | 3.29 | 1.35 | 1.11 |
| 14:45 | 1.88 | 1.82 | 2.63 | 1.98 | 1.41 | 2.89 | 1.05 | .869 |
| 15:15 | 1.59 | 1.35 | 2.14 | 1.60 | 1.21 | 2.39 | .734 | .705 |
| 15:45 | 1.32 | 1.17 | 1.69 | 1.18 | 1.03 | 1.82 | .438 | .409 |

## TABLE 4

## AVERAGE INCOMING 335-345-nm RADIATION (W/M$^2$) FOR 30-MINUTE INTERVALS IN 1966-7

| | DOWNTOWN WASH. D. C. | | | STERLING VIRGINIA | | | GAITHERSBURG MARYLAND | |
|---|---|---|---|---|---|---|---|---|
| TRUE SOLAR TIME | MAR. 3 | MAR. 27 | MAR. 30 | MAR. 3 | MAR. 27 | MAR. 30 | DEC. 12 | DEC. 15 |
| 8:45 | 1.44 | 2.03 | 2.17 | 1.69 | 1.80 | 2.48 | .804 | .943 |
| 9:15 | 1.71 | 2.51 | 2.68 | 2.26 | 2.36 | 2.96 | 1.12 | 1.16 |
| 9:45 | 2.07 | 2.64 | 3.10 | 2.47 | 2.91 | 3.43 | 1.43 | 1.47 |
| 10:15 | 2.23 | 2.89 | 3.58 | 2.99 | 2.64 | 3.84 | 1.71 | 1.75 |
| 10:45 | 2.85 | 3.38 | 3.69 | 3.31 | 2.51 | 4.00 | 1.93 | 2.01 |
| 11:15 | 3.24 | 3.38 | 3.83 | 3.52 | 2.45 | 3.97 | 2.10 | 2.16 |
| 11:45 | 3.27 | 3.31 | 3.30 | 3.40 | 2.81 | 4.10 | 2.20 | 2.23 |
| 12:15 | 3.19 | 2.44 | 4.14 | 3.33 | 2.72 | 4.17 | 2.21 | 2.20 |
| 12:45 | 3.14 | 2.45 | 4.15 | 3.30 | 2.28 | 4.25 | 2.14 | 2.10 |
| 13:15 | 3.03 | 2.77 | 3.95 | 3.15 | 2.35 | 4.02 | 2.00 | 1.94 |
| 13:45 | 2.75 | 2.46 | 3.67 | 2.89 | 2.29 | 3.83 | 1.76 | 1.70 |
| 14:15 | 2.35 | 2.29 | 3.29 | 2.60 | 2.14 | 3.58 | 1.50 | 1.45 |
| 14:45 | 2.06 | 1.93 | 2.82 | 2.18 | 1.52 | 3.17 | 1.19 | 1.13 |
| 15:15 | 1.81 | 1.45 | 2.29 | 1.77 | 1.32 | 2.64 | .836 | .803 |
| 15:45 | 1.58 | 1.26 | 1.82 | 1.34 | 1.14 | 2.03 | .517 | .484 |

### TABLE 5

### AVERAGE INCOMING 345-355 nm RADIATION ($W/M^2$)

### FOR 30-MINUTE INTERVALS IN 1966-7

| | DOWNTOWN WASH. D. C. | | | STERLING VIRGINIA | | | GAITHERSBURG MARYLAND | |
|---|---|---|---|---|---|---|---|---|
| TRUE SOLAR TIME | MAR. 3 | MAR. 27 | MAR. 30 | MAR. 3 | MAR. 27 | MAR. 30 | DEC. 12 | DEC. 15 |
| 8:45 | 1.63 | 2.27 | 2.44 | 1.89 | 2.00 | 2.76 | .905 | 1.04 |
| 9:15 | 1.93 | 2.82 | 3.01 | 2.55 | 2.63 | 3.30 | 1.26 | 1.28 |
| 9:45 | 2.31 | 2.98 | 3.48 | 2.78 | 3.25 | 3.81 | 1.61 | 1.61 |
| 10:15 | 2.54 | 3.19 | 3.99 | 3.34 | 2.94 | 4.27 | 1.92 | 1.93 |
| 10:45 | 3.23 | 3.79 | 4.13 | 3.77 | 2.77 | 4.45 | 2.14 | 2.21 |
| 11:15 | 3.63 | 3.81 | 4.16 | 3.93 | 2.70 | 4.40 | 2.37 | 2.38 |
| 11:45 | 3.67 | 3.71 | 2.94 | 3.79 | 3.10 | 4.55 | 2.47 | 2.46 |
| 12:15 | 3.59 | 2.77 | 4.65 | 3.73 | 3.01 | 4.64 | 2.49 | 2.42 |
| 12:45 | 3.55 | 2.72 | 4.67 | 3.71 | 2.52 | 4.73 | 2.41 | 2.31 |
| 13:15 | 3.42 | 3.08 | 4.48 | 3.54 | 2.60 | 4.48 | 2.25 | 2.14 |
| 13:45 | 3.08 | 2.74 | 4.13 | 3.18 | 2.53 | 4.27 | 1.99 | 1.87 |
| 14:15 | 2.66 | 2.56 | 3.70 | 2.96 | 2.37 | 4.00 | 1.68 | 1.60 |
| 14:45 | 2.32 | 2.16 | 3.17 | 2.46 | 1.68 | 3.54 | 1.35 | 1.25 |
| 15:15 | 2.04 | 1.61 | 2.58 | 2.00 | 1.47 | 2.94 | .947 | .889 |
| 15:45 | 1.78 | 1.41 | 2.05 | 1.52 | 1.27 | 2.26 | .588 | .541 |

### TABLE 6
### AVERAGE INCOMING 355-365-nm RADIATION (W/M$^2$)
### FOR 30-MINUTE INTERVALS IN 1966-7

| | DOWNTOWN WASH. D. C. | | | STERLING VIRGINIA | | | GAITHERSBURG MARYLAND | |
|---|---|---|---|---|---|---|---|---|
| TRUE SOLAR TIME | MAR. 3 | MAR. 27 | MAR. 30 | MAR. 3 | MAR. 27 | MAR. 30 | DEC. 12 | DEC. 15 |
| 8:45 | 1.76 | 2.47 | 2.65 | 1.99 | 2.12 | 2.93 | .963 | 1.10 |
| 9:15 | 2.11 | 3.09 | 3.28 | 2.68 | 2.79 | 3.50 | 1.35 | 1.36 |
| 9:45 | 2.54 | 3.39 | 3.78 | 2.94 | 3.45 | 4.06 | 1.72 | 1.72 |
| 10:15 | 2.71 | 3.67 | 4.35 | 3.53 | 3.11 | 4.53 | 2.06 | 2.06 |
| 10:45 | 3.51 | 4.18 | 4.50 | 4.04 | 2.92 | 4.72 | 2.34 | 2.37 |
| 11:15 | 3.88 | 4.15 | 4.51 | 4.19 | 2.84 | 4.68 | 2.55 | 2.55 |
| 11:45 | 3.92 | 4.00 | 4.14 | 4.01 | 3.27 | 4.84 | 2.65 | 2.63 |
| 12:15 | 3.85 | 3.13 | 5.08 | 3.95 | 3.18 | 4.93 | 2.67 | 2.59 |
| 12:45 | 3.83 | 2.93 | 5.05 | 3.92 | 2.64 | 5.02 | 2.58 | 2.47 |
| 13:15 | 3.69 | 3.30 | 4.86 | 3.79 | 2.74 | 4.75 | 2.41 | 2.29 |
| 13:45 | 3.33 | 2.94 | 4.48 | 3.42 | 2.66 | 4.55 | 2.11 | 2.00 |
| 14:15 | 2.80 | 2.75 | 4.02 | 3.19 | 2.50 | 4.24 | 1.80 | 1.70 |
| 14:45 | 2.51 | 2.33 | 3.43 | 2.63 | 1.77 | 3.79 | 1.46 | 1.37 |
| 15:15 | 2.21 | 1.72 | 2.81 | 2.19 | 1.54 | 3.13 | 1.00 | .951 |
| 15:45 | 1.92 | 1.51 | 2.19 | 1.68 | 1.34 | 2.40 | .619 | .580 |

## TABLE 7

## AVERAGE INCOMING 365-375-nm RADIATION (W/M$^2$) FOR 30-MINUTE INTERVALS IN 1966-7

| | DOWNTOWN WASH. D. C. | | | STERLING VIRGINIA | | | GAITHERSBURG MARYLAND | |
|---|---|---|---|---|---|---|---|---|
| TRUE SOLAR TIME | MAR. 3 | MAR. 27 | MAR. 30 | MAR. 3 | MAR. 27 | MAR. 30 | DEC. 12 | DEC. 15 |
| 8:45 | 2.02 | 2.82 | 3.02 | 2.34 | 2.45 | 3.41 | 1.12 | 1.26 |
| 9:15 | 2.40 | 3.54 | 3.75 | 3.18 | 3.22 | 4.06 | 1.56 | 1.55 |
| 9:45 | 2.88 | 3.70 | 4.29 | 3.42 | 4.02 | 4.70 | 1.99 | 1.96 |
| 10:15 | 3.02 | 3.96 | 4.94 | 4.13 | 3.59 | 5.24 | 2.38 | 2.35 |
| 10:45 | 3.99 | 4.74 | 5.08 | 4.69 | 3.33 | 5.44 | 2.70 | 2.70 |
| 11:15 | 4.47 | 4.65 | 5.12 | 4.82 | 3.24 | 5.38 | 2.93 | 2.90 |
| 11:45 | 4.50 | 4.51 | 4.81 | 4.66 | 3.72 | 5.56 | 3.05 | 2.99 |
| 12:15 | 4.37 | 3.56 | 5.75 | 4.55 | 3.62 | 5.68 | 3.06 | 2.95 |
| 12:45 | 4.32 | 3.30 | 5.71 | 4.50 | 3.00 | 5.77 | 2.96 | 2.80 |
| 13:15 | 4.16 | 3.70 | 5.51 | 4.36 | 3.12 | 5.42 | 2.76 | 2.59 |
| 13:45 | 3.78 | 3.30 | 5.06 | 3.95 | 3.03 | 5.22 | 2.43 | 2.27 |
| 14:15 | 3.14 | 3.08 | 4.55 | 3.11 | 2.85 | 4.88 | 2.05 | 1.92 |
| 14:45 | 2.82 | 2.62 | 3.88 | 3.02 | 2.01 | 4.35 | 1.68 | 1.51 |
| 15:15 | 2.41 | 1.95 | 3.17 | 2.45 | 1.75 | 3.60 | 1.15 | 1.07 |
| 15:45 | 2.00 | 1.70 | 2.50 | 1.87 | 1.54 | 2.76 | .708 | .655 |

## TABLE 8

## AVERAGE INCOMING [illegible]-nm RADIATION (W/M$^2$)
## FOR 30-MINUTE INTERVALS IN 1966-7

| | DOWNTOWN WASH. D. C. | | | STERLING VIRGINIA | | | GAITHERSBURG MARYLAND | |
|---|---|---|---|---|---|---|---|---|
| TRUE SOLAR TIME | MAR. 3 | MAR. 27 | MAR. 30 | MAR. 3 | MAR. 27 | MAR. 30 | DEC. 12 | DEC. 15 |
| 8:45 | 2.08 | 2.90 | 3.13 | 2.37 | 2.52 | 3.51 | 1.15 | 1.28 |
| 9:15 | 2.49 | 3.66 | 3.87 | 3.27 | 3.30 | 4.17 | 1.61 | 1.57 |
| 9:45 | 3.06 | 3.80 | 4.42 | 3.50 | 4.13 | 4.83 | 2.06 | 1.99 |
| 10:15 | 3.15 | 4.05 | 5.12 | 4.16 | 3.65 | 5.41 | 2.48 | 2.40 |
| 10:45 | 4.18 | 4.87 | 5.23 | 4.82 | 3.39 | 5.59 | 2.81 | 2.75 |
| 11:15 | 4.67 | 4.75 | 5.08 | 4.94 | 3.28 | 5.53 | 3.04 | 2.96 |
| 11:45 | 4.70 | 4.62 | 4.80 | 4.71 | 3.79 | 5.72 | 3.17 | 3.05 |
| 12:15 | 4.54 | 3.83 | 5.99 | 4.64 | 3.69 | 5.83 | 3.17 | 3.01 |
| 12:45 | 4.49 | 3.39 | 5.88 | 4.64 | 3.04 | 5.93 | 3.08 | 2.86 |
| 13:15 | 4.36 | 3.80 | 5.68 | 4.46 | 3.17 | 5.55 | 2.87 | 2.65 |
| 13:45 | 3.95 | 3.39 | 5.22 | 4.04 | 3.08 | 5.35 | 2.53 | 2.31 |
| 14:15 | 3.29 | 3.13 | 4.69 | 3.71 | 2.91 | 5.01 | 2.13 | 1.96 |
| 14:45 | 2.96 | 2.67 | 4.01 | 3.08 | 2.03 | 4.46 | 1.75 | 1.54 |
| 15:15 | 2.58 | 1.99 | 3.27 | 2.44 | 1.78 | 3.68 | 1.18 | 1.09 |
| 15:45 | 2.22 | 1.75 | 2.58 | 1.91 | 1.56 | 2.82 | .726 | .66[illegible] |

## TABLE 9

## AVERAGE INCOMING 385-395-nm RADIATION (W/M$^2$) FOR 30-MINUTE INTERVALS IN 1966-7

| | DOWNTOWN WASH. D. C. | | | STERLING VIRGINIA | | | GAITHERSBURG MARYLAND | |
|---|---|---|---|---|---|---|---|---|
| TRUE SOLAR TIME | MAR. 3 | MAR. 27 | MAR. 30 | MAR. 3 | MAR. 27 | MAR. 30 | DEC. 12 | DEC. 15 |
| 8:45 | 2.12 | 2.96 | 3.17 | 2.43 | 2.56 | 3.57 | 1.17 | 1.26 |
| 9:15 | 2.55 | 3.75 | 3.93 | 3.31 | 3.33 | 4.24 | 1.64 | 1.56 |
| 9:45 | 3.10 | 3.89 | 4.49 | 3.57 | 4.17 | 4.92 | 2.10 | 1.99 |
| 10:15 | 3.08 | 4.03 | 5.24 | 4.27 | 3.67 | 5.51 | 2.52 | 2.43 |
| 10:45 | 4.18 | 4.86 | 5.30 | 4.90 | 3.41 | 5.69 | 2.78 | 2.75 |
| 11:15 | 4.72 | 4.79 | 5.72 | 5.02 | 3.29 | 5.64 | 3.09 | 2.95 |
| 11:45 | 4.88 | 4.64 | 5.13 | 4.15 | 3.80 | 5.82 | 3.22 | 3.04 |
| 12:15 | 4.58 | 4.08 | 6.13 | 4.76 | 3.70 | 5.94 | 3.23 | 2.99 |
| 12:45 | 4.49 | 3.24 | 5.96 | 4.69 | 3.05 | 6.04 | 3.12 | 2.85 |
| 13:15 | 4.34 | 3.78 | 5.74 | 4.54 | 3.18 | 5.61 | 2.91 | 2.64 |
| 13:45 | 3.95 | 3.41 | 5.28 | 4.13 | 3.09 | 5.41 | 2.57 | 2.30 |
| 14:15 | 3.32 | 3.14 | 4.76 | 3.78 | 2.93 | 5.09 | 2.17 | 1.95 |
| 14:45 | 2.99 | 2.67 | 4.07 | 3.15 | 2.04 | 4.51 | 1.80 | 1.52 |
| 15:15 | 2.60 | 1.99 | 3.31 | 2.56 | 1.78 | 3.73 | 1.19 | 1.07 |
| 15:45 | 2.25 | 1.75 | 2.60 | 1.99 | 1.57 | 2.86 | .724 | .651 |

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