length dependence of the quantum yield for photooxidation, not observed in those for fluorescence and phosphorescence. They concluded that electron ejection competes with thermal equilibration of the first excited singlet state. Thus in the rigid glass TMPD solution the electron ejection is a relatively fast process taking place, preferentially, from high vibrational levels. In aqueous solutions of $\beta$-naphthol it seems that this picture of vibronic photochemistry cannot be adopted. Electron ejection competes here with fluorescence emission so that $k_e$ and $k_e'$ should be of the same order of magnitude as $k_f$ and $k_f'$, *i. e.*, $k_e \cong k_e' = 10^7$–$10^8$ sec.$^{-1}$.

These results should also be compared with those previously obtained by us[1-4] in the study of electron ejection from the solvated halide ions in their C.T.T.S. excited states. In these systems the excited state consists of an expanded electronic orbital centered by the respective halogen atom.[15,16] Electron ejection in this case consists of charge asymmetrization giving place to the separated solvated electron–halogen atom pair.[4] This is essentially a process of relative diffusion and thus faster by several orders of magnitude than the electron ejection in the case of excited $\beta$-naphthol or naptholate, where electron ejection competes with a relatively slow deactivation.

(15) R. L. Platzman and J. Franck, "Farkas Memorial Volume," Jerusalem, 1952, p. 21.

(16) G. Stein and A. Treinin, *Trans. Faraday Soc.*, **55**, 108b (1959).

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# The Fluorescence of Carbon Disulfide Vapor

BY JULIAN HEICKLEN

For incident radiation between 2800 and 3600 Å., the primary process in $CS_2$, is given in eq. 2–4. The total emission between 4200 and 6500 Å. was measured. It was found that reaction 4 occurs on every collision, and that $k_3 = 3.0 \times 10^5$ sec.$^{-1}$. Results with added biacetyl are similar; the electronic energy is removed by collision and not transferred as such to the biacetyl.

## Introduction

Apparently the emission from gaseous $CS_2$ has not been reported previously. The purpose of this paper is to establish the mechanism associated with luminescence.

The absorption spectrum has been obtained at high resolution by Lieberman[1] and Kleman.[2] More recently, a small note showing the absorption profile has appeared.[3] The first absorption starts at about 3600 Å., passes through a maximum near 3200 Å., and extends to 2600 Å.

## Experimental

The optical equipment used to measure fluorescence is shown schematically in Fig. 1. The light source is an Osram-type XBO 1600 lamp. This high-pressure xenon lamp operates at 1600 w. and emits continuous radiation from 2000 Å. to the infrared region. The light is focused by a quartz lens onto the entrance slit of a Perkin-Elmer Model 98 monochromator and is spectrally dispersed by a Bausch and Lomb grating No. 33–53–09–29 which is blazed at 5000 Å. and has 1800 grooves per mm. The monochromator was calibrated with the line spectrum of a medium-pressure Hanovia mercury arc. This arc was used to measure the dispersion also.

After passing through a quartz lens, a Corning 7-54 filter, and a diaphragm opening, the radiation enters the fluorescence cell. The purpose of the lens is to focus the light at the center of the cell, whereas the filter removes any scattered radiation above 4000 Å.

The T-shaped stainless-steel cell is 5.0 cm. long and 2.5 cm. in diameter. The side arm extends 1.3 cm. and is also 2.5 cm. in diameter. Sapphire windows are mounted with "Eccobond 26" epoxy glue at both ends and on the side arm. A 6-mm. outlet at the top of the cell connects, through a stopcock, to an adjoining high-vacuum line.

The transmitted radiation is focused by a quartz lens onto an RCA 935 phototube. An ASCOP 541B-03 photomultiplier, operated at 1500 v., collects the fluorescent radiation that has left the side arm and has passed through a Wratten 2E filter. The filter transmits radiation above 4200 Å. and the photomultiplier is sensitive to 6500 Å.

(1) L. N. Lieberman, *Phys. Rev.*, **58**, 183 (1940); **59**, 106 (1941); **60**, 496 (1941).

(2) B. Kleman, Symposium of Molecular Structure and Spectroscopy, Columbus, Ohio, June, 1956.

(3) E. Treiber, J. Gierer, J. Rehnstrom, and K. E. Almin, *Acta Chem. Scand.*, **11**, 752 (1957).

The materials used were Allied Chemical C.P. grade $CS_2$ and Eastman Kodak White Label biacetyl. Pressures were measured on an alphatron which had been calibrated previously against a Wallace and Tiernan direct-reading pressure gage.

The absorption coefficients of $CS_2$ were measured at various wave lengths and with slit openings of 0.500 and 2.000 mm. Because the radiation was not truly monochromatic, the measured absorption coefficients are not necessarily constant with pressure if the absorption is large. Thus, the coefficients were obtained over the range of pressures which resulted in absorption of more than a few per cent. If less than about 10% of the light is absorbed, then the measured absorption coefficients become truly independent of pressure, because the quantity $\exp(-\epsilon_\lambda C l)$ in the Beer's law expression can be approximately by $1 - \epsilon_\lambda C l$. Here $\epsilon_\lambda$ is the absorption coefficient for wave length $\lambda$, $C$ is the concentration, and $l$ is the path length.

When pure $CS_2$ was studied, the fluorescent radiation was computed as the difference of the photomultiplier output with the cell full and empty. For $CS_2$–biacetyl mixtures, the background reading was measured when the cell contained the appropriate pressure of biacetyl. In this way, the correction is automatically made for the biacetyl emission. Readings were taken at eight wave lengths with slit openings of both 0.500 and 2.000 mm.

## Results

The results with pure $CS_2$ are given in Table I and Fig. 2 and 3. In all cases, only the emitted light above 4200 Å. and below 6500 Å. was collected. The relative emission yield (emission per photon absorbed) for a given incident wave length $Q_\lambda$ was measured at various pressures and two different slit-width settings.

In Table I, the ratios of the relative emission yields at various incident wave lengths to the emission yield with incident radiation centered at 3213 Å. are shown. There are three important observations to be made from Table I. These are: (1) Within the limits of the fairly large scatter of the data, there is no discernible trend in the values of the ratios with change in pressure. This is true even though the pressure has been varied by a factor of greater than $10^5$ and the individual relative emission yields vary by a factor of about $10^4$. The scatter in the data is most pronounced at the lowest pressures where the total emitted light was smallest. The average values of the ratios and the mean deviations are also listed in Table I. (2) Within

### TABLE I
### RELATIVE FLUORESCENCE EFFICIENCIES FOR CS₂

| Press., mm. | $Q_{2884}/Q_{3213}$ | $Q_{2968}/Q_{3213}$ | $Q_{3050}/Q_{3213}$ | $Q_{3132}/Q_{3213}$ | $Q_{3297}/Q_{3213}$ | $Q_{3380}/Q_{3213}$ | $Q_{3462}/Q_{3213}$ |
|---|---|---|---|---|---|---|---|
| | | | Slit width 500 μ | | | | |
| $0.90 \times 10^{-3}$ | .. | .. | 1.24 | 0.95 | 1.14 | .. | .. |
| $2.1 \times 10^{-3}$ | .. | .. | 1.06 | 0.74 | 0.55 | .. | .. |
| $6.2 \times 10^{-3}$ | .. | 1.56 | 1.06 | 0.74 | 0.55 | .. | .. |
| $15.5 \times 10^{-3}$ | .. | 2.16 | 1.70 | 1.50 | .79 | .. | .. |
| 0.033 | 3.10 | 1.95 | 1.49 | 1.23 | .93 | 1.14 | 1.45 |
| .087 | 1.38 | 1.68 | 1.57 | 1.28 | .97 | 1.08 | 1.12 |
| .122 | 4.15 | 2.07 | 1.65 | 1.30 | .93 | 1.21 | 1.51 |
| .141 | 3.06 | 2.19 | 1.71 | 1.30 | .96 | 0.69 | .. |
| 1.40 | 2.26 | 2.67 | 1.51 | 1.28 | .89 | 1.02 | 1.17 |
| 12.5 | 2.71 | 2.12 | 1.71 | 1.39 | .98 | 1.28 | 1.68 |
| 129 | 2.58 | 1.64 | 1.70 | 1.64 | .85 | 1.00 | 1.75 |
| Av. | 2.75 ± 0.45 | 2.01 ± 0.26 | 1.53 ± 0.17 | 1.26 ± 0.17 | 0.90 ± 0.10 | 1.06 ± 0.15 | 1.45 ± 0.20 |
| | | | Slits = 2000 μ | | | | |
| $1.07 \times 10^{-3}$ | .. | .. | 1.05 | 0.96 | 1.61 | .. | .. |
| $2.3 \times 10^{-3}$ | .. | .. | 1.06 | 1.04 | 1.18 | .. | .. |
| $6.4 \times 10^{-3}$ | .. | 2.56 | 1.31 | 1.22 | 0.94 | 0.89 | .. |
| $15.5 \times 10^{-3}$ | .. | 1.69 | 1.35 | 1.18 | .97 | 1.00 | 1.63 |
| 0.033 | 2.11 | 1.85 | 1.40 | 1.25 | .95 | 0.93 | 1.41 |
| .087 | 2.26 | 2.29 | 1.99 | 1.55 | 1.21 | .80 | 1.02 |
| .122 | 3.18 | 2.01 | 1.61 | 1.30 | 1.03 | .98 | 1.58 |
| .141 | 2.33 | 2.05 | 1.61 | 1.27 | 0.86 | .94 | 0.83 |
| 1.40 | 2.10 | 3.07 | 1.66 | 1.28 | .76 | 1.01 | 1.47 |
| 12.5 | 2.53 | 2.34 | 1.53 | 1.25 | .80 | 0.82 | 1.47 |
| 129 | 2.13 | 2.06 | 1.77 | 1.61 | .82 | 0.74 | 1.14 |
| Av. | 2.38 ± 0.19 | 2.21 ± 0.31 | 1.49 ± 0.23 | 1.26 ± 0.12 | 1.01 ± 0.18 | 0.90 ± 0.08 | 1.32 ± 0.24 |

experimental error, the emission yield ratios are the same with slit widths of 0.500 or 2.000 mm. even though the absorbed intensity differs by a factor of 16. (3) The emission yield between 4200 and 6500 Å. is greatest with incident radiation centered at 2884 Å. It decreases to a broad minimum with incident radiation centered at about 3300 Å. and then rises at longer incident wave lengths.

ASCOP 541B-03 PHOTOMULTIPLIER — QUARTZ LENS — RCA 935 PHOTOTUBE — WRATTEN NO. 2E FILTER — FLUORESCENCE CELL — CORNING 7-54 FILTER — DIAPHRAGM — QUARTZ LENS — XENON LAMP — MONOCHROMATOR
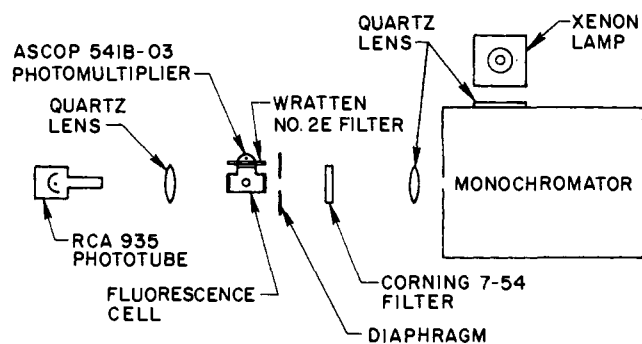
Fig. 1.—Schematic diagram of top view of optical equipment.

Figure 2 is a plot of reciprocal relative emission yield vs. pressure for various incident wave lengths and for pressures up to 150 μ. Within experimental error the curves are linear with nonzero intercepts.

Figure 3 is a log–log plot of the reciprocal relative emission yield minus the appropriate intercept from Fig. 2 vs. the pressure. The straight line of slope unity which best fits the points has been drawn in. It is seen that such a line satisfactorily represents the experimental data.

The radiative lifetime $\tau$ of the initially formed excited state can be estimated from the absorption coefficients $\epsilon_\lambda$ through the relationship

$$\int \epsilon_\lambda \, d\nu = \frac{1}{8\pi c \nu^2 n^2} \frac{g_u}{g_l} \frac{1}{\tau} \qquad (1)$$

where $c$ is the velocity of light; $\nu$, the wave number, in cm.⁻¹, of the absorption band; $n$, the refractive index of the medium; and $g_u$ and $g_l$ are the multiplicities of the upper and lower states, respectively. The quantities $n$, $g_u$, and $g_l$ are all unity. Thus, from our measured absorption coefficients $1/\tau$ is found to be $3.1 \times 10^5$ sec.⁻¹.

2884 Å.   2968 Å.   3050 Å.   3132 Å.   3213 Å.   3297 Å.   3380 Å.   3462 Å.

○ 2000-mm SLIT WIDTH
• 0.500-mm SLIT WIDTH
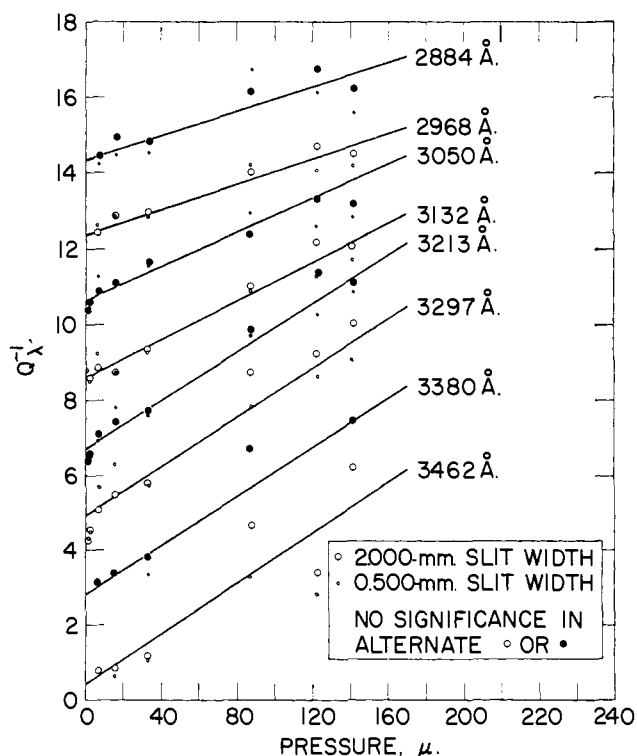NO SIGNIFICANCE IN ALTERNATE ○ OR •

$Q_\lambda^{-1}$    PRESSURE, μ.

Fig. 2.—Plots of $Q_\lambda^{-1}$ in arbitrary units vs. the CS₂ pressure for various incident radiations. The ordinate scale is based on data with incident radiation at 3462 Å. The other plots are raised successively by two units to eliminate confusion.

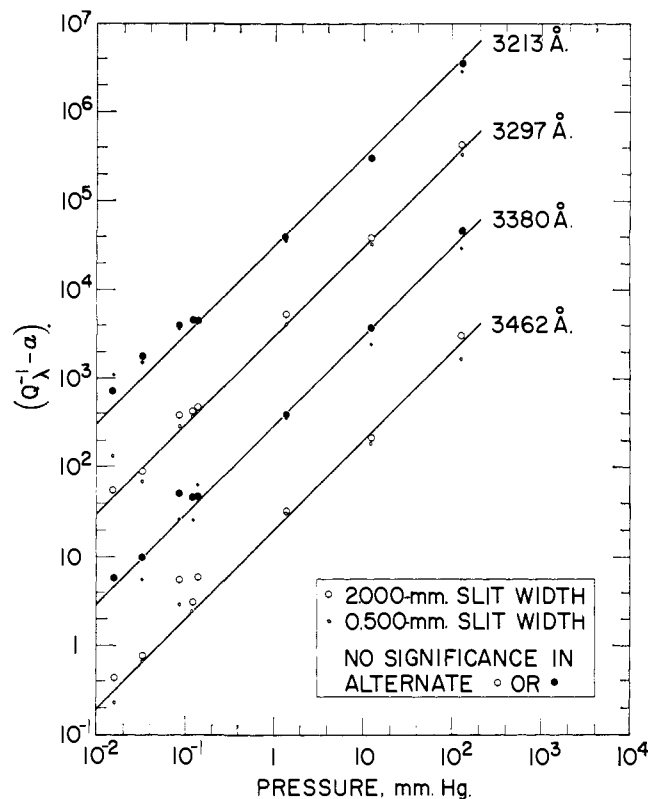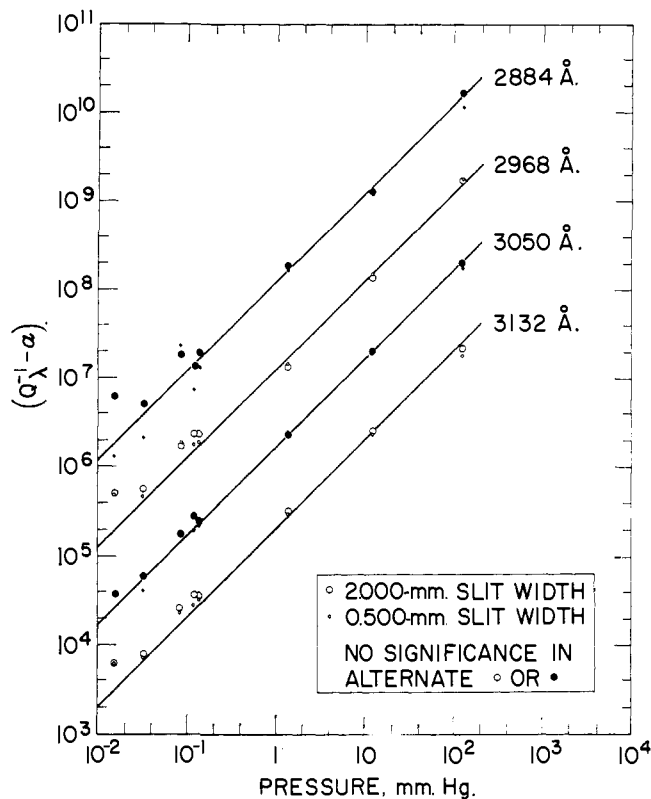A few runs were done in which mixtures of CS₂ and biacetyl were irradiated. It is well known that

Fig. 3.—Log–log plots of $Q_\lambda^{-1} - \alpha$ in arbitrary units vs. the $CS_2$ pressure for various incident radiations.   The ordinate scale is based on data with incident radiation centered at 3462 Å.   The other plots are raised successively by factors of 10 to eliminate confusion.

carbonyl-containing compounds readily transfer electronic energy to biacetyl,[4] and it was desired to see if $CS_2$ also could transfer its energy to biacetyl. The results indicated that no such transfer occurred and that biacetyl quenched the emission at about the same rate (or perhaps slightly more efficiently) as $CS_2$.

## Discussion

None of the incident wave lengths is energetic enough to lead to photodecomposition. Therefore, the fact that the emission efficiency for radiation between 4200 and 6500 Å. varies with incident wave length shows that vibrational equilibration does not occur before emission, for if equilibration did occur, the fluorescence spectrum, and thus the emission yield, would be independent of the exciting wave length. In fact, the data in Table I show that there is no tendency to vibrational equilibration of the excited state even at higher pressures. These results can be explained only if *every* collision leads to electronic deactivation.

As expected, when the absorption coefficient is largest (*i.e.*, in the region of 3000 to 3300 Å.), the likelihood of resonant fluorescence is highest. Thus, at these incident wave lengths, relatively less radiation is emitted above 4200 Å. than when the incident radiation corresponds to the wings of the absorption curve.

The simplest mechanism which explains the facts is

$$CS_2 + h\nu \longrightarrow CS_2^* \qquad (2)$$
$$CS_2^* \longrightarrow CS_2 + h\nu' \qquad (3)$$
$$CS_2^* + CS_2 \longrightarrow 2CS_2 \qquad (4)$$
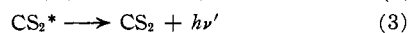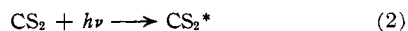
where $CS_2^*$ represents a vibrationally excited level of the upper electronic state. The degree of vibrational excitation depends on the incident energy. There

(4) H. Okabe and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **79**, 801 (1957); J. Heicklen and W. A. Noyes, Jr., *ibid.*, **81**, 3858 (1959); E. Murad, *J. Phys. Chem.*, **64**, 942 (1960); D. S. Weir, *J. Am. Chem. Soc.*, **84**, 4039 (1962); J. Dubois, *ibid.*, **84**, 4041 (1962); R. Borkowski and P. Ausloos, *ibid.*, **84**, 4044 (1962); J. L. Michael and W. A. Noyes, Jr., *ibid.*, **85**, 1027 (1963).

might also be a first-order deactivating step not associated with light emission, but there is no evidence that such a step is needed. When biacetyl is present, it, as well as the $CS_2$, can deactivate by collision. The fact that there is no intensity effect under our conditions eliminates the possibility of excited molecule–excited molecule reactions. However, under flash conditions, such reactions are undoubtedly important and lead to the observed photochemical decomposition.[5]

The mechanism predicts the relationship

$$\frac{1}{Q_\lambda'} = 1 + \frac{k_4}{k_3}(CS_2) \qquad (5)$$

where $Q_\lambda'$ is the absolute emission yield and is directly proportional to the relative emission yield.

$$Q_\lambda' = \alpha Q_\lambda \qquad (6)$$

Thus

$$Q_\lambda^{-1} = \alpha + \frac{\alpha k_4}{k_3}(CS_2) \qquad (7)$$

Figure 2 shows plots of $Q_\lambda^{-1}$ vs. the $CS_2$ pressure. These plots are linear in conformity with eq. 7, and the slopes and intercepts are listed in Table II for the various incident wave lengths.

### TABLE II
#### EVALUATION OF RATE CONSTANTS

| Incident radiation, Å. | $\alpha k_4/k_3$, mm.$^{-1}$, from Fig. 2 | $\alpha$ from Fig. 2 | $\alpha k_4/k_3$, mm.$^{-1}$, from Fig. 3 | $k_4/k_3$ mm.$^{-1}$ |
|---|---|---|---|---|
| 2884 | 16.5 | 0.30 | 11.8 | 39 |
| 2968 | 17.2 | .35 | 12.4 | 35 |
| 3050 | 22.8 | .65 | 16.4 | 25 |
| 3132 | 26.0 | .58 | 20.0 | 35 |
| 3213 | 32.6 | .70 | 30 | 43 |
| 3297 | 33.0 | .92 | 30 | 33 |
| 3380 | 32.8 | .84 | 29 | 35 |
| 3462 | 34.0 | .43 | 20 | 46 |
|  |  |  | Av. | 36 ± 5 |

(5) F. Wright, *J. Phys. Chem.*, **64**, 1648 (1960).

At very low pressures, it is possible that wall effects could become important. Simple kinetic theory calculations show that for pressures below about 50 $\mu$, collisions with the wall start competing with intermolecular collisions; below 10 $\mu$, wall collisions would predominate. Thus, if wall collisions were important, the plots in Fig. 2 would "flatten out" at low pressure. It is easily seen that this does not occur. Kinetic theory calculations also show that the time required to reach the wall in the absence of intermolecular collisions is about $10^{-5}$ to $10^{-4}$ sec. Since wall reactions are unimportant, the lifetime of the excited state at zero pressure must be less than $10^{-5}$ sec. or $k_3$ must exceed $10^5$ sec.$^{-1}$. The value of $k_3$ found from the integrated absorption coefficient is $3.1 \times 10^5$ sec.$^{-1}$ in agreement with the above.

Equation 7 can be rewritten

$$\log (Q_\lambda^{-1} - \alpha) = \log \left( \frac{\alpha k_4}{k_3} \right) + \log (CS_2) \qquad (8)$$

Figure 3 shows log–log plots of $Q_\lambda^{-1} - \alpha$ vs. $(CS_2)$ where the values of $\alpha$ used are the intercepts of Fig. 2.

The data fit linear plots of slope unity. The intercepts give $(\alpha k_4/k_3)$, and these are listed in Table II. The values of $\alpha k_3/k_2$ from Fig. 3 are similar to but somewhat different from those in Fig. 2. The values from Fig. 3 are much more accurate because they result from plots covering a pressure range of $10^4$.

The ratio $k_4/k_3$ is found by dividing the quantity $\alpha k_4/k_3$ obtained from Fig. 3 by $\alpha$ as obtained from Fig. 2. These values are listed in the fifth column of Table II. It is interesting to note that even though $\alpha$ and $\alpha k_4/k_3$ vary by a factor of three for various incident wave lengths, the ratios are constant to within about 20%. The average value of $k_4/k_3$ is $36 \pm 5$ mm.$^{-1}$.

Since every collision deactivates, $k_4$ can be estimated from kinetic theory. Using a reasonable collision diameter of 5 Å., one finds that $k_4$ becomes $1.0 \times 10^7$ (mm.-sec.)$^{-1}$. This gives a value for $k_3$ of $2.9 \pm 0.4 \times 10^5$ sec.$^{-1}$ in excellent agreement with that of $3.1 \times 10^5$ sec.$^{-1}$ found from the integrated absorption coefficient.

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# The Radiolysis of Methanol and Methanolic Solutions. II. Comparison of Radiolysis by Co60 γ-Rays and by B10(n,α)Li7 Recoils[1]

BY MASASHI IMAMURA, SANG UP CHOI, AND NORMAN N. LICHTIN

At recoil dose rates in the vicinity of $4.5 \times 10^{15}$ e.v. ml.$^{-1}$ min.$^{-1}$ $G(H_2) = 4.99 \pm 0.36$, $G(CH_4) = 0.57 \pm 0.14$, $G(CO) = 1.00 \pm 0.13$, $G(CH_2O) = 3.15 \pm 0.38$, $G(C_2H_6O_2) = 0.60 \pm 0.09$, independent of dose over the range $(0.44–10.8) \times 10^{19}$ e.v. ml.$^{-1}$ and of dose rate over the range $(0.33–25) \times 10^{15}$ e.v. ml.$^{-1}$ min.$^{-1}$. All yields are insensitive to added KI up to 0.1 $M$. The effects of change in LET by a factor of $10^3$ are rationalized tentatively on the basis that there is little variation in initial relative abundance of primary radical and molecular products but that reactions of higher than first order in primary radicals are of increased importance. Satisfactory reproducibility in the Co60 γ-radiolysis of "pure" methanol was not obtained in this work and its achievement remains a problem. Alkali fluorides, chlorides, and bromides all reduce $G(H_2)$ but have no significant effects on other yields. Alkali iodides also reduce $G(H_2)$ from Co60 γ-radiolysis and, in addition, decrease $G(C_2H_6O_2)$ and increase $G(CH_2O)$ by equal amounts without significant formation of iodine. This observation can be rationalized by the coupled reduction of $CH_3O$ and oxidation of $CH_2OH$ by I$^-$ and I, respectively, as proposed by Theard and Burton.

## Introduction

This paper describes a limited investigation of the effect of variation of LET on the radiolysis of liquid methanol at room temperature. Unfortunately, the results must be interpreted with more than the usual degree of caution because satisfactory reproducibility of yields from the γ-radiolysis of "pure" methanol does not appear to have been achieved as yet. Recently, Baxendale and Mellows[2] presented evidence indicating that they had obtained reproducible results from "pure" methanol. We have, however, not been able to duplicate their results nor did Theard and Burton.[3,4]

Recently reported yields from the γ-radiolysis of methanol are presented in Table I along with a few relevant earlier data.[5–10] That differences among yields cannot be correlated systematically with the methods of

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission under Contract AT(30-1)2383.

(2) J. H. Baxendale and F. W. Mellows, *J. Am. Chem. Soc.*, **83**, 4721 (1961).

(3) L. M. Theard, "Radiolysis of Liquid Methanol and Some Methanolic Solutions," Dissertation submitted to Graduate School of Notre Dame University, March, 1961.

(4) L. M. Theard and M. Burton, *J. Phys. Chem.*, **67**, 59 (1963).

(5) R. H. Johnsen, *ibid.*, **65**, 2144 (1961).

(6) N. N. Lichtin, *ibid.*, **63**, 1449 (1959).

(7) S. U. Choi, this report.

(8) M. Imamura, this report.

(9) E. Hayon and J. J. Weiss, *J. Chem. Soc.*, 3970 (1961).

(10) E. Hayon and J. J. Weiss, *ibid.*, 3962 (1961).

analysis is illustrated for the gaseous products. Values of $G(H_2)$ appear to fall in three ranges, around 5.4, 4.6–5.0, and 4.0–4.1.[11,12] Baxendale and Mellows[2] have concluded that the smallest values arise from adventitious complete scavenging of a reactive precursor of hydrogen, presumed to be the solvated electron. This conclusion is consistent with the fact that either no[9–11] purification procedure or a questionable one[12] was employed where $G(H_2) = 4.1$ was obtained. Apparently carefully purified methanol has given values falling in the remaining two regions. Values of $G(CH_4)$ vary over a factor of almost three. Burton and Theard[3,4] have shown that complete removal of methane from methanol is difficult and, perhaps, the two or three lower values of $G(CH_4)$ reflect failure to collect this product quantitatively. The highest values of $G(CH_4)$ are associated with the highest values of $G(H_2)$, however, suggesting that a chemical factor is involved. Reproducibility of $G(CO)$ should be expected to be poor because of its low value. There appears to be no correlation between values of $G(CO)$ or $G(CH_2O)$ and those of $G(H_2)$. $G(CH_2O)$ is apparently approximately 2.1 and is not highly sensitive to the adventitious impurities common to methanol. If the values of Johnsen[5] and of Hayon and Weiss[9] are discarded, values of $G$-(glycol) fall into two groups. Values around $3.0^{4,6–8,11,12}$

(11) W. R. McDonell and S. Gordon, *J. Chem. Phys.*, **23**, 208 (1955).

(12) G. E. Adams and J. H. Baxendale, *J. Am. Chem. Soc.*, **80**, 4215 (1958).