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PHOTOCHEMICAL STUDIES IN FLASH PHOTOLYSIS

IV. INTENSITY AND WAVELENGTH EFFECTS

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SUMMARY

Wavelength and intensity effects which we have observed in the flash photolysis of acetone are reviewed. Marked nonmonotonic wavelength effects occurred in the different regions investigated (260, 280 and 300 mμ) and serve to emphasize the problem of interpreting any data obtained with unfiltered light. The data at 300 mμ were compared with those obtained with continuous light sources 10^6 fold less intense. A considerable difference occurred in the C_2H_6/CO ratio. To investigate this intensity effect, flash photolyses were made over a wide range of reduced intensities, as low as 10^4 fold less than the maximum one, and the transition intensity region for change in C_2H_6/CO ratio and CO quantum yield was located. This phenomenon illustrates the more general fact that the apparent primary processes observed at *typical* flash intensities need not be the same as the primary processes found at low intensities.

INTRODUCTION

Since its advent around 1950, many studies have appeared on flash photolysis, mostly to obtain large concentrations of radicals for spectroscopic examination, but also for photochemical studies based on analysis of reaction products. In most of these investigations the aim was to produce a high light intensity for this condition meant high radical concentrations. Since the use of optical filters reduces this intensity appreciably, relatively few studies have employed them.

At this conference we would like to describe some wavelength and intensity effects which we have observed in our photochemical studies of the flash photolysis of acetone. One may expect that the general nature of these results and the precautions they imply will apply to other flash photolysis systems as well.

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WAVELENGTH EFFECTS

In initial photochemical studies on the flash photolysis of acetone in various laboratories, quartz vessels were employed without filters ([1 2 3]). Under these conditions, none of the reaction products were proportional to the acetone pressure ([2, 3]) a result due to the intense absorption peaks of acetone near 190 and 195 mμ ([4]). This intense absorption compensated for the relatively lower intensity of the incoming light in this wavelength region. When the radiation below 200 mμ was removed by a suitable cellophane filter, the CO production became directly proportional to the acetone pressure ([2]).

In a further study ([5]), the flash photolysis of acetone was examined using the full spectrum of the flash but with the radiation below 200 mμ eliminated. The quantum yields were independent of the light intensity and the C_2H_6/CO ratio decreased with increasing acetone pressure in a curious manner : The ratio first decreased, then levelled off, then finally at higher acetone pressures decreased again, towards unity. As pointed out elsewhere ([6]), the results resembled a composite curve which arose from several excited states. It was decided, therefore, to study wavelength effects in some detail.

In a recent study using a series of filters transmitting radiation centered at 260, 280, 300 and (with a few runs) 310 mμ, with half-width of typically 20 mμ, very marked effects occurred ([7]). In all cases, at the light intensities employed, the quantum yields were independent of incident intensity and the C_2H_6/CO ratio decreased with increasing acetone pressure. However, although the ratio of CO/(acetone pressure) was independent of acetone pressure around 260 mμ and 300 mμ, it increased appreciably with pressure at 280 mμ. Such an increase had been previously observed, though over a narrower pressure range, with flash photolysis employing the essentially monochromatic light (280 mμ) of a magnesium spark discharge ([8]). The results of the two investigations ([7 8]) were in quite good agreement, except for the lowest pressure point (50 mm) of Ref. 8.

This decrease of C_2H_6/CO ratio, in conjunction with the other results, was explained ([5]) in terms of the deactivation of excited molecules. (The proposed reaction mechanism is given below.) From Stern-Volmer plots, the intrinsic lifetimes of the excited acetone molecules were estimated to be 0.6×10^{-9}, 1×10^{-9} and 4×10^{-9} sec at 260, 280 and 300 mμ respectively, assuming a collisional deactivation efficiency of unity. At low pressures, where there is relative freedom from deactivation effects, the $\mathrm{C_2H_6/CO}$ ration was about 3.2, 5.6 and 1.9 at 260, 280 and 300 mμ, a nonmonotonic function of wavelength. In one other difference between these various wavelengths, the $\mathrm{C_2H_6/CO}$ ratio fell to near unity at high acetone pressures at 280 and 300 mμ but not at 260 mμ.

A detailed discussion of deductions made from these and other results has been given elsewhere (7). It was pointed out that the following apparent processes may occur in all the wavelength regions :

$$
\begin{aligned}
\mathrm{(CH_3)_2\,CO} + h\nu &\rightarrow \mathrm{2CH_3 + CO}\\
&\rightarrow \mathrm{(CH_3)_2\,CO^*} \rightarrow \mathrm{CH_3CO + CH_3}\\
&\qquad\qquad\qquad \overset{\rightarrow}{\mathrm{M}}\ \mathrm{(CH_3)_2CO},
\end{aligned}
$$

where M is any molecule, acetone for example. The word apparent is emphasized since as described later our CO formation in the above reaction at 300 mμ arises in large measure from an excited molecule.

It appears too that at 280 mμ there occurs in addition some collision induced dissociation (7 8)) :

$$\mathrm{(CH_3)_2CO^* + M \rightarrow 2CH_3 + CO + M},$$

and, at 260 mμ, an additional primary process :

$$\mathrm{(CH_3)_2CO} + h\nu \rightarrow \mathrm{CH_3CO + CH_3}$$

The results at 280 mμ indicate that the effects of wavelength cannot be interpolated in general.

Although unreactive gases have sometimes been used to moderate the temperature rise caused by the flash, the above pressure effects show that they must be used with caution, if at all, because of possible deactivation. Fortunately, at the reduced intensities obtained by use of filters, the temperature rise was estimated (7) to be 5 °C or less, a truly negligible increase.

INTENSITY EFFECTS

Since the results in the previous section were intensity independent, some comparison with the photochemical data obtained from non-flash low intensity sources is appropriate. In the literature, data with acetone have been obtained at 254 and 313 mμ. For purposes of comparison with these studies and with our flash photolysis data, we have been obtaining data around 300 mμ, as well as around 260 and 280 mμ, using an AH6 lamp and other sources, employing the filters used in the flash study. In this brief note we shall restrict our remarks to the 300 mμ region.

At low intensities (CO production rate of the order of 10^{-13} and 10^{-12} moles cm^{-3} sec^{-1} in Refs. 9 and 7, respectively) and proceeding to 0.01% conversion the C_2H_6/CO ratio at 50 mm acetone was 1.7 and 1.9 respectively. This ratio which equals roughly [(biacetyl)/CO] + 1 shows that biacetyl, and hence CH_3CO, is formed to a major extent under these conditions. The corresponding C_2H_6/CO ratio under flash conditions at 50 mm acetone and 0.01% conversion (CO production rate of the order of 10^{-6} moles cm^{-3} sec^{-1}) in the 300 mμ region is 1.1 to 1.2, so that CH_3CO formation is minor. This difference surprised us (perhaps it should not have), for it showed that at flash intensities not all of the apparent primary processes were the actual ones. At these high intensities, a simple computation shows (7) that a long-lived excited acetone molecule, such as the phosphorescent one studied by Kaskan and Duncan (10), having a lifetime of the order of 2×10^{-4} sec, will undergo a number of collisions with similarly long lived excited species and with free radicals under our conditions. To explain the intensity independence of the quantum yields observed under the flash conditions such a reaction had to be complete if it occurred at all.

A major problem of our investigation, therefore, involved locating the transition region of intensities where C_2H_6/CO fell from its high value a low intensities to its low value a flash intensities, a region lying somewhere in the millionfold difference of the two intensities. For this purpose, our first apparatus, which employed an exploding wire source, was abandoned in favor of one using a flash lamp, permitting a large number of repetitive low intensity flashes and being completely auto-

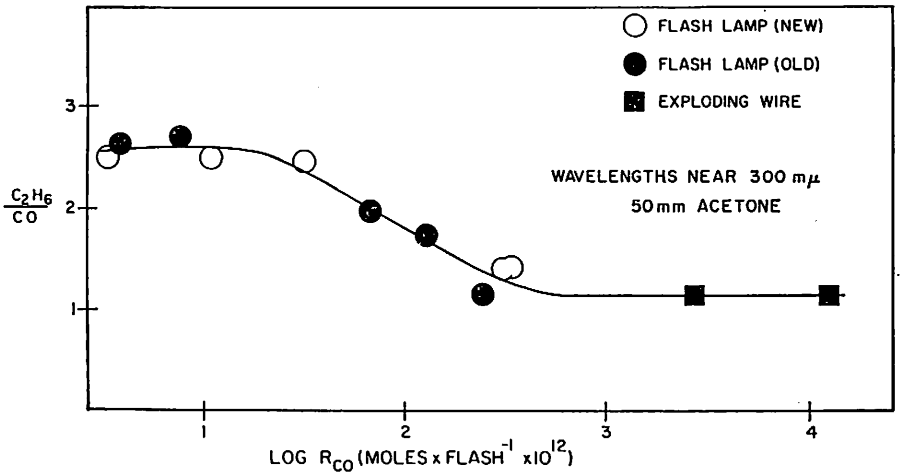

Fig. 1 — Effect of light intensity, I_a, on the C_2H_6/CO ratio. $I_a = R_{CO}/\Phi_{CO}$, where relative Φ_{CO}'s are given in Table 1.

matic. The incident light intensity was varied by changing the lamp-vessel distance. The flash time for exploding wire and lamp was about 100 μ sec in each case (7).

TABLE 1

Photolysis of Acetone (50 mm) at wavelengths near 300 mμ[a].

Expt.	$\frac{C_2H_6}{CO}$	R^{rel}_{CO}	I^{rel}_{a}	Φ^{rel}_{CO}	Φ^{rel}_{Biac}
37	1.4	1	1	1	0.4
38	1.4	0.94	—	—	—
35	1.6	0.56	0.83	0.67	0.4
36	2.4	0.099	0.25	0.40	0.5_6
39	2.4	0.031	0.082	0.38	0.5_3
40	2.5	0.0105	0.028	0.38	0.5_4

[a] R^{rel}_{CO} and I^{rel}_{a} refer to the respective values divided by the values of Expt. 37. $\Phi^{rel}_{CO} = R^{rel}_{CO}/I^{rel}_{a}$. Φ^{rel}_{Biac} denotes $\Phi_{Biac}/\Phi_{CO\ \#\ 37}$ where $\Phi_{CO\ \#\ 37}$ is the presently unknown value of Φ_{CO} in expt. # 37. Φ^{rel}_{Biac} equals $R_{Biac}/R_{CO} \times \Phi^{rel}_{CO}$. We have assumed that $R_{Biac} = R_{C_2H_6} - R_{CO}$. (See ref. 7 for measurements of R_{Biac} at high intensities). The light source used was a G.E. flash lamp FT-503 which was powered by a 30 μ F condenser charged to 4000 V. The duration of the flash was measured by means of a 935 RCA phototube and a calibrated oscilloscope and was found to be 0.1 msec. The reaction vessel, described in ref. 7, was surrounded by a 5 cm I.D. Vycor jacket which in turn was surrounded by a 9 cm O.D. Vycor cylinder around which was wrapped a single layer of du Pont Cellophane 88-CA-48. The space between the inner and outer Vycor cylinder contained $NiSO_4$-$CoSO_4$ solution (40 grams of each in 100 cc water). The effective light path of this solution was 1.3 cm. The center of the flash lamp coincided with a point 11 cm (8 cm in expts. 37 and 38) from bottom of reaction vessel. The light intensity was varied by altering the distance between the center of the lamp and center of reaction vessel. This distance in the respective experiments was as follows : Expt. 37-8.5 cm; 38-9 cm; 35-9 cm; 36-17.5 cm; 39-32.5 cm; 40-56.5 cm. Methods of analysis and actinometry (concentration employed here being 5×10^{-5} M) are described in ref. 7.

The data are given in Table 1 and figure 1, where it will be seen that at the lowest intensities the C_2H_6/CO is about 2.6. This value is relatively close, in terms of biactyl/CO ratio ($=C_2H_6/CO - 1$), to that found with continuous light sources at intensities 100-fold less. In addition, a transition region occurs at intensities about 100-fold less than the usual flash intensities. The fact that the C_2H_6/CO at 300 mμ is constant at very high and at very low flash intensities but changes from one value to the other at intermediate intensities (Table 1 and, for higher intensities, ref. 7) can be interpreted in terms of the following scheme :

$$\begin{aligned} A + h\nu &\rightarrow A^* \\ 2A^* &\rightarrow 2CH_3 + CO + A \qquad (a) \\ A^* &\rightarrow A \end{aligned}$$

where A denotes acetone and A* is another of its excited states.

However, another possible path for this extra CO production at high intensities is given by (*b*) :

$$A^* + CH_3CO \rightarrow A + CH_3 + CO \qquad (b)$$

If reaction (*a*) prevails $\Delta\Phi_{CH_3CO}$ will be zero while if reaction (*b*) occurs instead, $\Delta\Phi_{CH_3CO}$ will equal $-\Delta\Phi_{CO}$ (Δ is the increase from the low intensity value as the intensity is increased). The Φ_{Biac} data tentatively suggest that reaction (*a*) is to be preferred as an explanation of these data. More precisely, if one uses Wijnen's ([11]) equation,

$$R_{CH_3CO} = 2R_{(C_2H_6-CO)} + 1.65\, R_{C_2H_6}{}^{\frac{1}{2}}\, R_{(C_2H_6-CO)}{}^{\frac{1}{2}},$$

then the $\Phi^{rel}_{CH_3CO}$ $(=\Phi_{CH_3CO}/\Phi_{CO_{\#37}})$ values are found to be 2.2, 2.2, 1.8, 1.9, 2.4 for Expts. 40, 39, 36, 35, 37 respectively. According to Table 1 $\Delta\Phi^{rel}_{CO}$ is $+ 0.6$ on going from the lowest to the highest intensity in Table 1. Accordingly, one expects $\Delta\Phi^{rel}_{CH_3CO}$ to be either zero or -0.6. It does not appear to be -0.6, but the analytical error in measuring $R_{C_2H_6-CO}$ at low C_2H_6/CO ratios is appreciable. Any more conclusive decision as to choice between steps (*a*) and (*b*) should await the direct determination of Φ_{Biac}. Such a determination is now in progress.

From the curve given in figure 1 and discussed above, it would appear that the data obtained at the usual flash intensities need not reflect the actual processes occurring at very low intensities. At the usual flash intensities bimolecular reactions between long-lived excited states or between such excited states and free radicals may occur. To eliminate such reactions it may be necessary, as it was in the present study, to work with light intensities some 1000-fold less.

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