Light Intensity and Frequency as Determinants in the Comparative Studies of Budde Effect and Joshi Effect

JAGDISH PRASHAD*

Department of Chemistry, Meerut College, Meerut-250 001, India

The influence of frequency and intensity of light on the Budde effect and the Joshi effect has been studied in chlorine admixed with a little air and water vapour. It has been found that the Budde effect increased with both the frequency and the intensity I of the irradiating light. At a constant applied potential V, $-\%$ Δi is a linear function of the light frequency. At low V, $-\%$ Δi increases rapidly with I and attains saturation at large I. It has been shown that the Budde effect occurs due to the characteristic optical adsorption of the gas and is discriminated from the Joshi effect which may be a frequency or quantum effect rather than a consequence of the characteristic optical adsorption in the gas phase.

INTRODUCTION

The earlier workers[1–4] in the field of the Budde effect $(\Delta p)_{V=0}$ in halogens reported divergent results as regards the influence of the frequency and intensity of the irradiating light on $(\Delta p)_{V=0}$. Those[5–7] on the Joshi effect Δi, however, obtained consistant ones. Light frequencies below 5500 Å and above 5800 Å are special regions where the results are not compatible. The present study has been carried out in chlorine admixed with a little air and water vapour productive of both $(\Delta p)_{V=0}$ and $\%$ Δi, in these regions in order to discriminate between the two effects $(\Delta p)_{V=0}$ and Δi.

EXPERIMENTAL

The present investigation of the Budde effect was carried out in chlorine at 724 mm g 33°C admixed with air at 0.3 mm Hg and water vapour at 0.2 mm Hg in Siemens ozonizer by interposing coloured light filters, in place of W (cf. Fig. 1), having different transmission limits, between the reaction vessel and the sources of irradiation. The influence of the intensity of irradiation was also studied in the admixed chlorine at different intensities by varying the distance of the source of irradiation—a 100 watt 220 volt tungsten filament lamp, from the ozonizer. The inverse square law was assumed. The general experimental procedure adopted and the mode of observations recorded were similar to those reported earlier.[8]

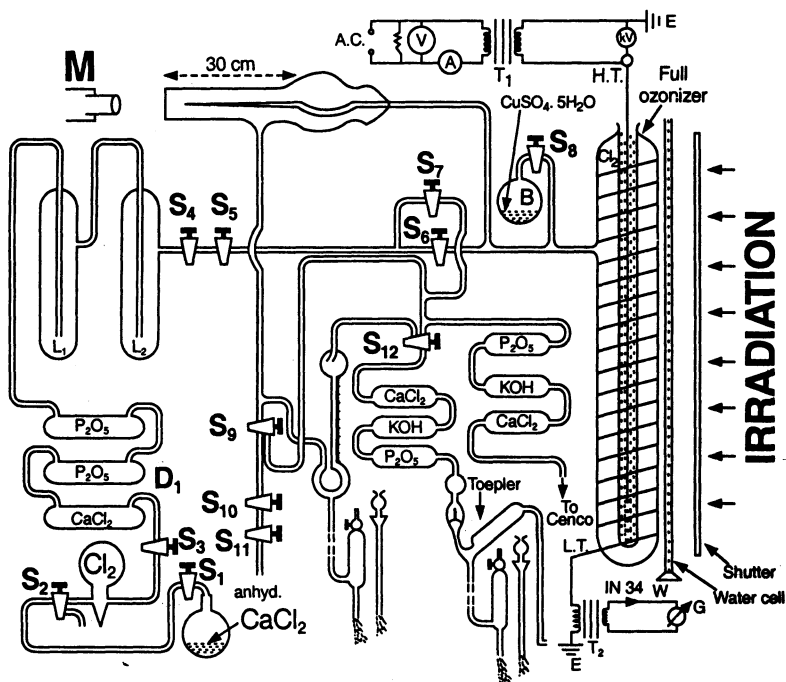*Mailing address   115, Krishanapuri, Meerut-250 002, India.

Fig. 1.   studies of Budde effect in Siemen's ozonizer.

Joshi effect in the range 3.74–7.48 kV was studied in the admixed chlorine under ozonizer excitation with the above-mentioned coloured filters as reported earlier.[9, 10]

The transmission spectrum of each of the filters used was determined by the optical methods. The following were the transmission limits of the coloured light filters used.

Filter	Transmission limits Å	Effective mean frequency $\times 10^{13}$
Blue	6400–3900	61.89
Yellow	6400–4300	58.03
Red	6400–5400	51.36

RESULTS AND DISCUSSION

The Budde effect increases with both the frequency as well as the intensity I of the irradiating light studied. The Joshi effect $-\%\ \Delta i$ increases with over bands ranging from red to blue. $-\%\text{-}\Delta i$ at a constant exciting potential V increases rapidly with I at low values of the latter. Further enhancement of I slows down this

increase in –% Δi which after characteristic value tends to become stationary (cf. Fig. 2).
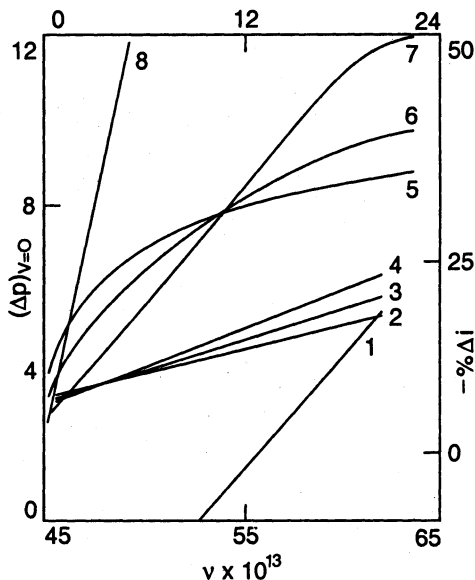

Fig. 2. Variation of Budde effect $(\Delta p)_{v=0}$ and Joshi effect Δi in admixed chlorine with frequency and intensity of light. [Curve 1: 1 : $(\Delta p)_{v=0}$ in scale divisions (1 division = 0.05 mm Hg) *vs.* effective mean frequency of light v; 2: –% Δi *vs.* v at 9.61 kV; 3: –% Δi *vs.* va$^+$ at 8.54 kV; 4: –% Δi *vs.* v at 6.41 kV; 5: –% Δi *vs.* relative light intensity I at 3.74 kV; 6: –% Δi *vs.* I at 5.34 kV; 7: –% Δi *vs.* I at 6.41 kV; 8: $(\Delta p)_{v=0}$ *vs.* I].

From the results of various workers,[11-13] it is evident that the absorption coefficient of chlorine increases with the frequency and is maximum in the ultraviolet region. Since the Budde effect is due to the characteristic light absorption in the continuum, the magnitude of the Budde effect should also increase with the frequency of light in the continuum. The present results are in accord with this. On the short wave side of 4785 Å, absorption of light leads to dissociation of chlorine molecules into one normal and one excited atom. Recombination of a normal chlorine atom with an excited one would result in the formation of an excited molecule. The increase of the Budde effect with increasing frequency thus follows.

The rate of photochemical formation of hydrogen chloride has usually been found to be proportional to the first power of the light intensity.[14] This is due to the fact that chlorine atoms formed by the process $Cl_2 + hv = 2Cl$ are used up as quickly as they are formed. Thus, the rate of reaction is determined by the rate of dissociation of chlorine which is proportional to the intensity of irradiation. Hence, the Budde effect is proportional to the light intensity.

That the threshold wavelength is fairly larger than the dissociation energy of molecules[15] suggests that Δi is probably a quantum effect determined entirely by

the absorption by the electrode layer rather than by the gas bulk. The threshold wavelength[16] for chlorine is 8100 Å and the wavelength corresponding to the dissociation energy of chlorine is 4785 Å. It is thus evident that the wavelength much longer than that coresponding to the dissociation energy of molecules can excite Δi.

This shows definitely that Harries and von Engel mechanism[17, 18] is untenable. The secondary electron emission is the consequence of τ and $\eta\theta g$ processes.[19] Whilst electron attachment would diminish the extent to which these processes occur, their enhancement is indepedent of the external light. $+\Delta i$ and the co-occurrance[20] of $-\Delta i$ and $+\Delta i$ cannot be accounted for on the mechanism of Harries and von Engel. Deo's observations[16] that $-\Delta i$ occurs in chlorine when irradiated with sodium light, which is must beyond to range of optical absorption, is in line with the present conclusion.

The linearity of the plot of log I *vs.* log % Δi indicates the applicability of Joshi-Lakshminarayanaiah's equation,[10] $\%\Delta i = aI^b$, to the case under study.

A possible explanation for the tendency to saturation of Δi at large I suggests itself from the activated electrode-layer-postulate.[21, 22] According to this, the formation of negative ion space charge results from the combination of gas particles with photo-electrons emitted from the boundary-layer under light. Moreover, the density of the space charge depends upon the magnitude of the primary photo-electron emission. With the increase in the light intensity, the electron emission will increase, as a consequence of which the space charge density will be enhanced. This will result in an increase in $-\Delta i$ as observed. The negative ions develop an opposing electrostatic field in the neighbourhood of wall-layer and lead to a slowing down of further emission and may, therefore, be responsible for the observed saturation in $-\Delta i$ at large I.

It is evident from the above discussion that the Budde effect which has been shown to be due to the characteristic optical absorption by the gas may now be discriminated from the Joshi effect which may be frequency or quantum effect rather than a consequence of the characteristic optical absorption in the gas phase.

ACKNOWLEDGEMENT

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