

A Light Effect in Chlorine under Electric Discharge: Influence of the Intensity and Frequency

FURTHER work on the diminution of the current which occurs on irradiation of chlorine^{1,2} has shown that several factors, some mutually exclusive, determine the magnitude of the phenomenon, such as the various electrical quantities; the electrode spacing, area and 'ageing' under the discharge; the nature of the gas, its temperature and especially the pressure. The chief difficulty in ascertaining the optimum conditions for the effect was that more than a limited variation of one of these altered others so much as to reduce the comparability of results. Furthermore, there was a limit to the influence of any of them on the decrease of current; for example, within a restricted pressure range and at a given applied potential, it increases to a maximum with decrease of pressure; it is negligible when the pressure is small. A similar limiting effect obtains with increase of applied potential at constant pressure.

Detailed studies of the above factors showed that a large Siemens' ozonizer, irradiated transversely and filled with about 11 c.c. of chlorine, was a fairly representative condition within the limitations of the electrical supply and especially the sensitivity of the available, oxide-rectifier type a.c. indicator. With a 50-cycle frequency, $v = 9,000$ volts (r.m.s.); a deflexion of 54 served to indicate the current. On irradiation by the carbon arc, the current decreased by 20–21 or about 38 per cent (see table); the decrease in the green and red was too small to measure accurately.

DECREASE OF CURRENT ON IRRADIATION

Light source	Wave-lengths (7800–3700 Å.)	White (7800–3700 Å.)	Violet (4750–4000 Å.)	Green (5775–5070 Å.)	Red (7070–6070 Å.)
200-watt bulb ..		10	8	0.5	1
Mercury arc ..		18	16	1	
Copper arc ..		9	7	0.5	
Carbon arc*		20	21	1	1
Iron arc*		20	20	1	0.5

* Due to the unsteadiness of these arcs, the comparative intensity conditions were not constant.

The effective frequency of irradiation was varied by use of coloured glass strips, instead of the Wratten or similar filters, due to the size of the ozonizer. It was limited on the short wave-length side at about 3700 Å. due to glass absorption. The intensity I was determined with a sensitive thermopile, a photo-electric cell and the corresponding spectrum. I_{green} in green was very low with all the sources used; this accounts for the corresponding decrease in current. With the bulb, the carbon and iron arcs, the decrease in the red is similar to that in the green. When, however, I_{red} was made comparable with I_{green} , the decrease in current due to the former was sensibly smaller and appeared attributable to the corresponding frequency difference. This factor also explains the comparatively large current decrease in the violet, although it is the narrowest of the bands employed; that this falls within the characteristic absorption of chlorine, namely, 2300–5000 Å.^{3,4} may well be an additional and important cause. It is interesting to note that the current decrease due to violet is comparable with that for the unfiltered,

that is, white light, where the total intensity is much greater.

The absorption coefficient of chlorine increases rapidly with frequency and is 65.5 at the band head, namely, 3340 Å. Its values at the short wave-length limits for the violet and the unfiltered white, namely, 4000 Å. and 3700 Å., are about 5 and 19 respectively^{3,4}; the corresponding growth of current decrease with frequency, however, is not of the same order (see table). A like result suggestive of saturation or some limiting condition is revealed by observations, over a wide intensity range of the ratio, of current decrease in white to that in the violet. This diminished from about 2 to 1 as the intensity was increased 2,200 times.

The above work was intended to form part of a comprehensive report of work, in progress since 1939, on what would appear to be a new photo-voltaic phenomenon in chlorine and other gases^{5,6}. Some typical results are indicated here, since it appears doubtful whether the work can be completed under present conditions.

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¹ Joshi and Narasimhan, *Curr. Sci.*, **9**, 537 (1930).

² Joshi and Deshmukh, *NATURE*, **147**, 806 (1941).

³ Halban and Siedentoff, *Z. phys. Chem.*, **103**, 71 (1922).

⁴ Elliott, *Proc. Roy. Soc., A*, **123**, 629 (1929).

⁵ Joshi and co-workers, *Proc. Ind. Sci. Cong.*, Pt. III (Chem. Sec.), Abst. 55–70 (1942).

⁶ Joshi, *Proc. Ind. Sci. Cong.*, pres. address to Chem. Sec. (1943).

The Hydrogen Bond and its Influence on Acid Strength

QUANTUM mechanical resonance is undoubtedly a determining factor in deciding acid strength in certain cases, and empirical relations sometimes exist between the number of possible resonance structures (taken as a measure of the resonance energy) and the logarithm of the dissociation constant¹.

The strengths of salicylic acid and 2 : 6 dihydroxybenzoic acid will be discussed here. There is first of all the difficulty of accounting for their strengths in terms of ions or dipoles, bond lengths, angles and simple electrical theory. An elementary analysis of the problem using the concept of electrostatic potential at the carboxyl ion, which is assumed to govern $\log K$, indicates that both acids have abnormally high ionization constants compared with benzoic acid. Also inspection shows that the two acids have similar strengths to chloroacetic and dichloroacetic acids, the ionization constants of which have already been accounted for on the resonance hypothesis.

Now it has been recognized for some time that internal hydrogen bond formation takes place in these phenolic derivatives² which is stronger in the ion than in the undissociated molecule, appreciably diminishing the proton capacity. It was thus of interest to see whether any relation existed between the number of resonance structures (n) (taking into account the hydrogen bonding) which could reasonably be formulated for these acid ions and the free energy of ionization. The accompanying table contains the relevant data, K being the thermodynamic ionization constant. With $n = 1$, we are dealing with