Transient Changes in the Potential of the Ag–AgI Electrode induced by a Light Pulse

EXPOSURE of a silver–silver iodide electrode in an electrolyte solution to a flash of light causes transient changes in the electrode potential. This effect is a function of the concentration of potential-determining ions, I⁻ and Ag⁺, and has a minimum near the point of zero charge (p.z.c.).

We observed this photoelectrical effect studying the system Ag–AgI–electrolyte solution with saltbridge 0·1 M calomel electrode. The calomel electrode was protected against the possible influence of light. The electrolyte solution contained 0·1 M KNO_3 and a variable concentration of potential determining ions.

The silver iodide electrode was prepared according to Engel[1] by the direct reaction of iodine vapour with a silver rod; the thickness of the silver iodide layer was about 150 nm. The changes in cell e.m.f. were measured with a Keithley voltmeter-amplifier (input impedance 10^{10} Ω) and registered by a Honeywell graphic recorder type 110–R017–0019 and by a Tectronic scope type 503, equipped with a Polaroid camera. We used a Metz Mecablitz 502 electronic flash unit (120 W), giving flashes of about 1/1,000 s duration. The distance between flash and cell was about 10 cm.

The absence of errors caused by electric induction effects was checked by an experiment in which the flash source was covered by black paper during the flash. A polished silver electrode not covered with silver iodide appeared to be insensitive to the flash.
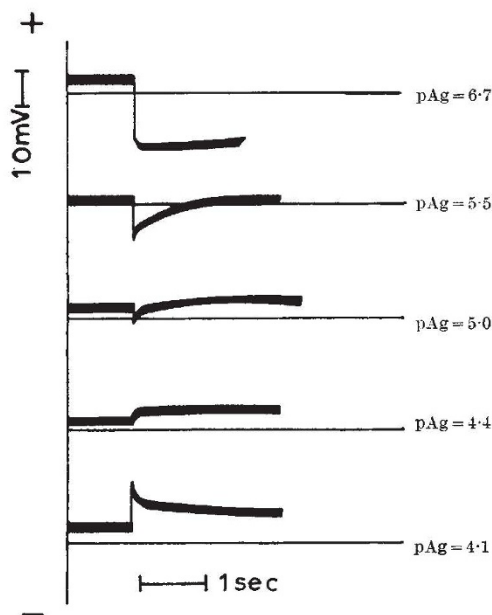

Fig. 1. Transient changes in the electrode potential due to a light pulse.

By exposing the silver iodide electrode in the galvanic cell to the flash we observed a fast deflexion from the equilibrium e.m.f., followed by a slow return to the original e.m.f. This effect depends on the pAg of the solution; the silver iodide electrode becomes transiently more positive at low pAg; the effect changes sign near the p.z.c. (pAg = 5·3) (see Fig. 1). The addition of urea (1·67 M) to the solution causes a shift of the effects to a lower pAg. Bijsterbosch[2] found a shift of the p.z.c. of the AgI/urea system in the same direction by a streaming potential technique.

Preliminary experiments with AgBr and CuI showed similar effects. The phenomena described may offer a new method for determining the point of zero charge of light-sensitive compounds.

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Charge-transfer-to-solvent Spectra

THE ultraviolet absorption spectra of simple inorganic anions contain intense (f about 0·1) broad structureless bands which have been characterized as charge-transfer-to-solvent transitions[1], or special cases of electron transfer spectra[2]. Detailed models[1,3,4] for these transitions treat the excited state as a radical and electron, with the latter in a centro-symmetric orbital on the solvent molecules surrounding the parent anion site. Such a transition would be represented by

$$X^-_{aq} \rightarrow (X\cdot + e^-)_{aq} \qquad (1)$$

The development of this theory has so far been restricted to the halide ions, and there is considerable disagreement about the detailed nature of the excited state[5]. The description of other anions in solution involves uncertainties which are so far unresolved[6].

Current theories suggest that E_{max}, the absorption maximum, should be related linearly to I_{X^-}, the ionization potential of the anion. In practice, however, for I_{X^-} less than 70 kcalories/mole, the experimental E_{max} tends to be independent of I_{X^-}, and when I_{X^-} is less than 50 kcalories/mole, E_{max} increases (Table 1).

Table 1. PARAMETERS OF IONS SHOWING C.T.T.S. TRANSITIONS

Ion	I_{X^-}	r_i (Å)	E_{max}		
			Water	Methyl cyanide	liq NH_3
I⁻$_{II}$	92·7	2·05	147·80	136·60	131·8
NO^-_2	90	1·81	—	150·00	—
Br⁻$_{II}$	88·3	1·80	150·00	146·50	—
Cl⁻$_{II}$	84·9	1·64	164·50	146·00	—
Cl⁻$_I$	82·5	1·64	162·10	143·6	—
N_3^-	80·0	2·04	140·0	129·3	—
Br⁻$_I$	77·9	1·80	141·5	131·7	—
I⁻$_I$	71·0	2·05	126·6	115·9	110·1
CNSe⁻	66·0	2·10*	121·8	111·4	—
CNTe⁻	59·0	2·35*	110·5	99·8	—
SH⁻	53·0	1·80	134·3	115·0	97·2
CNS⁻	49·9	1·95	132·6	122·3	114·4
OH⁻	40	1·53	153·3	—	—
NH^-_2	28	—	—	—	86·0

All values in kcalories mole⁻¹ unless indicated.
* Values assigned by reference to CNS⁻, ref. 6.
The subscripts I and II for the halides denote the $2p_{3/2}$ and $2p_{1/2}$ components of the observed doublets.

It therefore seems more plausible to suppose a simple shell-type acceptor orbital for the electron centred on the site of the parent anion and bounded by the solvent molecules. The anion is then to be regarded as an electron donor and the solvated anion as a donor–acceptor charge-transfer complex. The formalism developed by Mulliken[7] now leads to the transition energy

$$E_{max} = I_{X^-} - E_{solv} - C + \frac{\sigma^2}{I_{X^-} - E_{solv} - C} \qquad (2)$$

E_{solv} is the electron affinity of the solvent acceptor orbital —a cage of solvent molecules—and not that for isolated molecules.