CCCXVI.—*The Photochemical Oxidation of Alcohols by the Dichromate Ion.*

By EDMUND JOHN BOWEN and CHARLES WILLIAM BUNN.

THE photochemical oxidation of alcohols by the dichromate ion has been studied by Plotnikov (*Z. wiss. Phot.*, 1919, **19**, 40; *Z. Elektrochem.*, 1926, **32**, 13). The aim of the present work was to obtain measurements under as great a variety of conditions as possible, and to make measurements of the quantum efficiency.

Four lamps were used for different parts of the work : a 1000-c.p. Pointolite lamp, a 1000-watt tungsten-filament lamp, water-cooled, and two quartz–mercury lamps. Copper sulphate solution filters were used to remove infra-red and red radiation, and with the mercury lamps practically monochromatic radiation was obtained with Chance's black glass and cupriammonium sulphate filters.

The reactions were carried out in small quartz cells with plane-polished quartz ends fused on, the cells being fixed in a water thermostat electrically controlled. The energies of the radiations and the absorptions of the solutions were measured with a Moll thermopile calibrated in the usual way with a Hefner lamp.

The following two points were established in the first part of the work : (*a*) The chromate ion in neutral or alkaline solution is photochemically quite insensitive towards the alcohols. The results of Plotnikov (*loc. cit.*), that ammonium chromate is photoactive, are to be explained by partial hydrolysis to dichromate.

(*b*) The photochemical reaction between acid dichromate-ion solutions and alcohols leads to aldehyde formation without deposition of a precipitate. (In neutral solutions a precipitate is thrown down.) A series of measurements made with methyl alcohol solutions showed that the photochemical reaction curve obtained from the estimation of formaldehyde by the method of Schulek (*Ber.*, 1925, **58**, 732) was consistently 20% lower than that obtained from the decrease in dichromate-ion concentration. This was shown experimentally to be due to further oxidation of the formaldehyde, and the photochemical reaction may be represented :

$$Cr_2O_7'' + 8H^{\cdot} + 3CH_3{\cdot}OH \longrightarrow 3CH_2O + 2Cr^{\cdot\cdot\cdot} + 7H_2O.$$

In later experiments, the reaction was followed only by estimation of the dichromate-ion concentration, potassium iodide being added and the iodine titrated. The thermal reaction was followed at the same temperature, the reactants being contained in a blackened flask, and the true photochemical change was obtained by subtraction of the (small) thermal rate from the total rate in light.

The results of numerous experiments are summarised as follows. The quantum efficiency is independent of the following four factors : (1) light intensity, over a range of 1 : 80; (2) added acid, above a certain limit; (3) dichromate-ion concentration, between $N/10$ and $N/100$; and (4) temperature, between 15° and 50°.

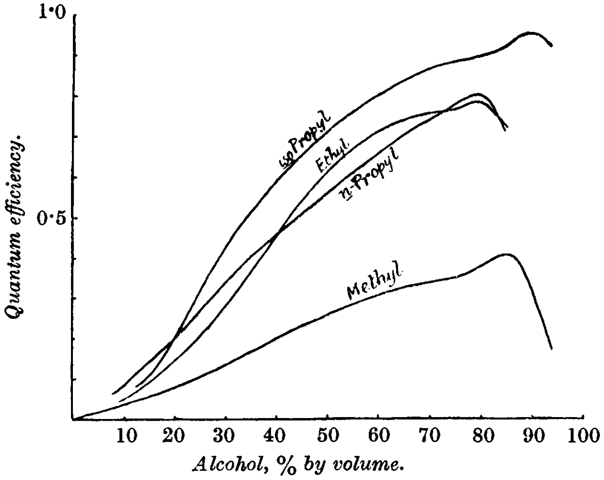
The photochemical reaction curves were determined for a series of alcohol–water mixtures at 15°, the dichromate-ion concentration being maintained at $N/20$ in each mixture, and the acid at $0{\cdot}2N$.

All the curves were linear over a large range of the first part of the reaction, and the slope gave the photochemical rates for the mixtures; these are summarised in Table I, the rates being expressed as the ratio of Cr_2O_7'' ions reduced to quanta absorbed, and plotted in Fig. 1.

TABLE I.

Methyl alcohol.		Ethyl alcohol.		*n*-Propyl alcohol.		*iso*Propyl alcohol.	
Alcohol, % by vol.	Photo-chemical rate.	Alcohol, % by vol.	Photo-chemical rate.	Alcohol, % by vol.	Photo-chemical rate.	Alcohol, % by vol.	Photo-chemical rate.
10	0·037	10	0·043	10	0·081	15	0·108
20	0·073	20	0·152	15	0·138	30	0·434
30	0·129	30	0·259	30	0·384	50	0·693
40	0·191	40	0·467	40	0·449	70	0·854
50	0·252	50	0·613	50	0·601	80	0·896
60	0·316	60	0·706	60	0·620	85	0·917
70	0·333	70	0·747	70	0·732	89	0·940
75	0·345	75	0·756	80	0·780	94	0·918
80	0·379	80	0·771	85	0·705		
85	0·400	85	0·714	89	0·606		
89	0·351						
94	0·162						
96	0 (fast dark reaction)						

FIG. 1.



As a check on these measurements, which were made in the light from a tungsten-filament lamp, filtered through copper sulphate solution, the quantum efficiency for the series of alcohols at concentrations equal to that of maximum rate was measured in monochromatic light from a quartz lamp: At 3666 Å., *Q.E.* of alcohol: methyl 0·45, ethyl 0·86, *n*-propyl 0·86, *iso*propyl 1·00. At 4200 Å. (approx.), ethyl alcohol 0·89. These results agree with the previous ones within the limit of error, if account be taken of the complete change of apparatus. The whole absorption band of the dichromate ion in the blue and violet region is therefore equally photoactive.

The variation of reaction rate with diminishing acid concentration was investigated and showed a regular decrease, but the results cannot be simply interpreted since the reaction occurs chiefly in the forward layers of the solution, producing variations in acidity throughout the cell. The reactions were also investigated in neutral solution. In this case, a precipitate is thrown down which is not chromium hydroxide, but which is capable of liberating iodine from potassium iodide. Owing to the scattering of the light by the precipitate, the rate falls off rapidly from the beginning of the exposure, and becomes zero when one-half of the total oxidising power of the dichromate solution is utilised. The simplest explanation of this is the formation of chromate :

$$Cr_2O_7'' + 3CH_3{\cdot}OH + H_2O \longrightarrow 3CH_2O + 2OH' + 2Cr(OH)_3.$$

$$2OH' + Cr_2O_7'' \longrightarrow 2CrO_4'' + H_2O.$$

The nature of the precipitate is obscure. Plotnikov has suggested that it is chromium chromate.

Owing to the falling off of the rate with time in the neutral reactions the initial rates for different alcohol–water mixtures were obtained by calculation from the curves. Table II summarises these initial rates, expressed for convenience as the ratio of rates acid/neutral for each mixture :

TABLE II.

Methyl alcohol.		Ethyl alcohol.		*n*-Propyl alcohol.	
Alcohol, % by vol.	Ratio of rates, $\frac{\text{acid}}{\text{neutral}}$.	Alcohol, % by vol.	Ratio of rates, $\frac{\text{acid}}{\text{neutral}}$.	Alcohol, % by vol.	Ratio of rates, $\frac{\text{acid}}{\text{neutral}}$.
30	2·77	20	2·06	15	2·2
50	2·92	30	2·15	30	2·87
70	2·80	40	2·85	50	3·3
80	2·93	50	3·1	70	3·28
82·5	2·89	70	3·2	80	3·08
85	2·62				
87·5	2·50				
90	3·0				

These measurements are not so accurate as those for acid solutions because of the uncertainty in the estimation of the initial rate. Since the ratio is practically constant, the curves for the neutral reactions are almost identical with those for the acid solutions except that the scale is about one-third. It seems that, whatever are the causes of the change in quantum efficiency with alcohol concentration, the same factors operate in acid and neutral solution.

Discussion of Results.

The results for acid solutions seem to point to the conclusion that the true quantum efficiency of the photochemical process is the decomposition of one dichromate ion and the oxidation of 3 molecules of alcohol per quantum absorbed. The measured quantum efficiency never reaches its true value because disturbing factors cause its diminution in mixtures containing excess of either alcohol or water. The diminution at high alcohol concentrations may be due to the appearance of a new substance, such as an alkyl chromate, since here the thermal reaction becomes very fast. If this is a correct deduction, it is improbable that the reaction really consists of the simultaneous collision of 3 alcohol molecules with an activated dichromate ion; and the simplest assumption is that the real photoactive substance is an alcoholated dichromate ion, *i.e.*, an ion with alcohol molecules attached by co-ordinate links. The diminution on the low alcohol concentration side would then be due to the equilibrium between non-photoactive hydrated dichromate ions and the photoactive alcoholated ions.

Applying the mass law as an approximation for the formation of a hydrate and an alcoholate, we have:

$$\frac{(Cr_2O_7)(H_2O)^n}{(Cr_2O_7,nH_2O)} = K_1; \quad \frac{(Cr_2O_7)(ROH)^m}{(Cr_2O_7,mROH)} = K_2.$$

Putting, for simplicity, $n = m$,

$$\frac{\text{Mol. fraction } H_2O}{\text{Mol. fraction ROH}} \times \sqrt[n]{\frac{(\text{alcoholate})}{(\text{hydrate})}} = K,$$

or roughly, at low alcohol concentrations:

$$\frac{\text{Mol. fraction } H_2O}{\text{Mol. fraction ROH}} \times \sqrt[n]{\text{Quantum efficiency}} = K.$$

The following calculations from the experimental data show that $n = 1$ approximately:

Methyl alcohol.

Alcohol, mols./l.	Mol. fraction H_2O/ROH × (quantum efficiency).
5·5	7·4
11	6·5
16	6·8
23	6·4
31	5·6

Ethyl alcohol.

Alcohol, mols./l.	Mol. fraction H_2O/ROH × (quantum efficiency).
3·3	14
7·1	20
11·4	21
16·9	23
23·6	18

n-Propyl alcohol.

Alcohol, mols./l.	Mol. fraction H_2O/ROH × (quantum efficiency).
3	25
4·5	29
9·5	35
14	28
19·4	24

*iso*Propyl alcohol.

Alcohol, mols./l.	Mol. fraction H_2O/ROH × (quantum efficiency).
4	26
9·2	43
19·4	27·6

In order to make the hypothesis fit the measurements, therefore, it must be assumed that only one molecule of alcohol or water is attached to each dichromate ion. It is hardly possible to accept this result, as it does not remove the difficulty of the oxidation of 3 molecules of alcohol per quantum absorbed.

An alternative hypothesis is that the activated dichromate ions have a mean " life " and only react if they collide with alcohol molecules during this " life." Applying an approximate equation (Grüss, *Z. Elektrochem.*, 1923, **29**, 144),

$$\text{Quantum efficiency} = 4\pi\sigma^2 nct/3v,$$

where v = number of volumes of solution containing one volume of alcohol; n = number of molecules in 1 c.c.; $\sigma = 10^{-8}$ cm.; c = velocity of dichromate ion; t = "life" of activated dichromate ion.

It is significant from the point of view of this hypothesis that the quantum efficiency for all the alcohols is approximately halved at a dilution of 1 : 3; whence $t = 3 \times 10^{-11}$ second.

This time is of the order of that required for an electron shift in a molecule, and is much shorter than the life of the activated molecules of chlorine (Grüss, *loc. cit.*) and iodine (Briers, Chapman, and Walters, J., 1926, 562). The result is not improbable, because the long life of activated halogen molecules may represent the time of recombination of atoms formed after activation. No dissociation of this kind is to be expected with the dichromate ion. The mechanism of the reaction, however, must still be considered to be very imperfectly understood.

Physical Chemistry Laboratory,
Balliol and Trinity Colleges,
Oxford.

[*Received, July* 11*th*, 1927.]