THE PHOTO-REDUCTION OF FERRIC CHLORIDE IN PRESENCE OF AQUEOUS ACETONE AND ANHYDROUS ETHER

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ALTHOUGH it is known that in admixed solutions with acetone ferric chloride is reduced in light (1) no work of a quantitative nature has yet been reported in literature. Some work, however, has been done on the photo-reduction of ethereal solutions of ferric chloride, but it lacks in thoroughness of treatment. Observations of a purely qualitative nature were made by Benrath (2), Puxeddu (3) and Spcier (4) using different regions of radiations as source of light. Later on, a quantitative study of the reaction was made by Puxeddu and Vodret (5) in sunlight as well as in arc light, but the method employed by them to estimate the amount of reduction is open to objection. They found that the reaction is of the first order and is completed in one hour. Further they found that the nature of the incident light has a marked effect on the reaction; at the same temperature the decomposition is much slower in arc light than in sunlight.

Talpade (6) has recently critically examined the applicability of various analytical reagents to estimate small quantities of ferrous iron in presence of large amounts of ferric iron and organic substance and has come to the conclusion that ceric sulphate is the only reagent which can be best employed for an unambiguous and direct measurement of a high degree of accuracy. The present investigation was therefore undertaken mainly with a view to obtain accurate quantitative data on the kinetics of the photo-reduction of ferric chloride in presence of aqueous acetone and anhydrous ether using ceric sulphate method for the estimation of the amount of reduction from time to time. The various effects on the reaction due to the changes in the concentration of ferric chloride, temperature, wave-length and the intensity of light have been studied and the quantum efficiency of the reactions has been also measured in light of different spectral regions at different temperatures with different concentrations of ferric chloride solutions.

Experimental

The source of light was a Phillip's 1000-watt vertical type cinema projector lamp worked at a constant current of 4·2 amps. The reaction cell

was made of optically plane parallel quartz plates; its capacity was 4·5 c.c. and internal thickness 5 mm. It was cemented at the top to a thick glass plate with two holes through which passed siphon tubes ground to the holes in the plate. To the siphon tubes were attached pieces of India rubber tubing which were closed air tight.

The light filters were Kodak's wratten filters. The mean wave-length transmitted in each case was determined spectroscopically and was found to be as follows:—

Blue filter	..	.. 4725 A.U.
Yellow filter	..	.. 5975 A.U.
Red filter	..	.. 6625 A.U.

Ferric chloride used was of A.R. quality obtained from B.D.H. It was dissolved in redistilled water with the addition of a certain amount of HCl in order to prevent the hydrolysis of ferric chloride (7) and also to stabilise the pH. Ethereal solutions of ferric chloride were prepared in Merck's extra-pure ether. Aqueous solutions of acetone were made by dissolving Merck's extra-pure quality acetone in redistilled water. These solutions were made in the dark and stored in air tight bottles which were always kept in a cool dry place.

After the elimination of heat radiations the parallel beam of light was incident on the reaction cell which was carefully screened from other radiations and was shaken from time to time to avoid the formation of " inner filters " (7). A Hilger thermopile connected to a Moll galvanometer recorded the intensity of the incident and the emergent beam of light. The absorbed energy was calculated from the galvanometer deflection differences for the reacting solution with and without ferric chloride, which were calibrated in terms of Hefner 100.

After insolating the mixture for a certain known interval, the cell was taken out of the thermostat and connected to a titration bottle and a wash bottle. On exhausting the air in the titration bottle the water from the wash bottle passed through the reaction cell to the titration bottle, thus draining the cell completely of its contents. The amount of reduction was determined by titrating the mixture against a standard solution of ceric sulphate with diphenylamine in sulphuric acid as. an internal indicator in the presence of a few c.c. of syrupy phosphoric acid.

The results obtained are given in the following tables in which

$a =$ the initial concentration of ferric chloride expressed in millimoles in 4 c.c. of the reaction mixture,

$b =$ the initial concentration of acetone expresesd in millimoles in 4 c.c. of the reaction mixture,

$T =$ the temperature at which the reaction is studied,

$I =$ the incident intensity in terms of galvanometer deflections,

$\lambda =$ the wave-length of the exciting radiations in A.U.,

$X =$ the amount of reduction of ferric chloride in millimoles in 4 c.c. of the reaction mixture,

$t =$ the time of exposure in minutes, and

$K =$ the unimolecular velocity constant.

TABLE I

Ferric Chloride and Aqueous Acetone

$b = 0 \cdot 2764 ; T = 35°.$

t	$a = 0 \cdot 8604$		$a = 0 \cdot 5736$		$a = 0 \cdot 2868$	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
60	6·12	1·151	4·05	1·190	2·12	1·228
120	12·06	1·170	7·96	1·190	4·18	1·247
180	17·86	1·164	11·88	1·177	6·26	1·228
240	23·58	1·161	15·88	1·180	8·28	1·228
300	29·36	1·159	19·66	1·174	10·26	1·220
360	35·19	1·158	23·49	1·164	12·24	1·209
480	46·44	1·156	31·18	1·171	16·06	1·204
600	57·60	1·155	38·70	1·170	19·80	1·194

TABLE II

Ferric Chloride and Anhydrous Ether

$T = 35°$

t	$a = 0 \cdot 9583$		$a = 0 \cdot 4863$		$a = 0 \cdot 2448$	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
60	7·92	1·381	4·14	1·420	2·34	1·573
120	15·84	1·381	8·28	1·439	4·64	1·573
180	23·54	1·381	12·33	1·420	6·84	1·561
240	31·14	1·372	16·29	1·420	9·04	1·554
300	38·52	1·366	20·16	1·412	11·12	1·543
360	45·99	1·369	24·12	1·414	13·23	1·541
480	60·93	1·367	31·86	1·410	17·46	1·545
600	75·60	1·370	39·60	1·416	21·60	1·539

It can be seen from the above tables that the photo-reduction of ferric chloride in the presence of acetone and ether is not a zeromolecular reaction because the values of X/t decrease steadily as the reaction proceeds. If the reaction is of the first order, then the time required for the completion of the same fraction of the reaction carried out with different initial concentrations should be the same. Different values of X/a for reactions started with different initial concentrations were therefore calculated and are given in the following table:

TABLE III

t	X/a for acetone			X/a for ether		
	$a = 0.8604$	0.5736	0.2868	0.9583	0.4863	0.2448
60	0.0071	0.0071	0.0074	0.008	0.009	0.010
120	0.0140	0.0139	0.0146	0.016	0.017	0.019
180	0.0208	0.0207	0.0218	0.025	0.025	0.028
240	0.0274	0.0277	0.0289	0.032	0.034	0.037
300	0.0341	0.0343	0.0358	0.040	0.042	0.045
360	0.0409	0.0410	0.0427	0.048	0.050	0.054
480	0.0540	0.0544	0.0560	0.064	0.066	0.071
600	0.0669	0.0675	0.0690	0.079	0.081	0.088

It will be seen from the above table that for the same period of insolation the values of X/a are very nearly independent of the initial concentration of ferric chloride. The photo-reduction of ferric chloride in presence of acetone and ether, therefore, is a unimolecular reaction. This is confirmed by the facts that (i) the plot of log $(a-X)$ against the time of insolation is a straight line, in all cases, and (ii) the values of the unimolecular velocity constants, given in Tables I and II, agree fairly well for a particular concentration of ferric chloride.

The mean values of the velocity constant for different initial concentrations of ferric chloride are given in the following table:

TABLE IV

a	Acetone			Ether		
	0.8604	0.5736	0.2868	0.9583	0.4863	0.2448
$K \times 10^4$	1.159.	1.177	1.220	1.373	1.419	1.554
		Mean ⟶ 1.185			Mean ⟶ 1.449	

It will be seen from the above table that the velocity constant decreases with increase in the concentration of ferric chloride, the deviations from the mean being beyond the experimental error.

The effect of temperature

The effect of temperature was examined by studying the kinetics of the reaction at 30° and 40° in addition to that studied at 35° in composite light. The results obtained are given in the following tables:

TABLE V

Ferric Chloride and Acetone

t	$a = 0.8604$		$a = 0.5736$		$a = 0.2868$	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
Temperature 30°						
60	5·40	1·036	3·42	0·998	1·94	1·113
120	10·71	1·036	6·72	0·998	3·74	1·074
180	15·75	1·023	9·99	0·985	5·40	1·062
240	20·97	1·027	13·27	0·988	7·16	1·065
Temperature 40°						
60	6·93	1·343	4·54	1·343	2·43	1·420
120	13·77	1·343	8·82	1·305	4·72	1·381
180	20·52	1·330	13·14	1·292	6·93	1·356
240	27·00	1·333	17·46	1·295	9·18	1·363

TABLE VI

Ferric Chloride in Ether

t	$a = 0.9583$		$a = 0.4863$		$a = 0.2448$	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
Temperature 30°						
60	7·34	1·266	3·92	1·343	2·15	1·458
120	14·49	1·266	7·52	1·305	4·23	1·439
180	21·51	1·253	11·25	1·292	6·21	1·420
240	28·35	1·257	14·85	1·295	8·19	1·420
Temperature 40°						
60	9·72	1·688	5·13	1·765	2·94	1·995
120	19·26	1·688	10·12	1·746	5·74	1·957
180	28·71	1·688	15·12	1·752	8·46	1·957
240	37·98	1·688	20·07	1·756	11·16	1·948

The effect of temperature on the velocity of the reaction is quite appreciable as will be seen from the following table which gives the mean values of the unimolecular velocity constants:

TABLE VII

| t | Mean values of $K \times 10^4$ for | | | | | |
| | Acetone | | | Ether | | |
	$a = 0.9604$	0.5736	0.2868	0.9583	0.4863	0.2448
30°	1.030	0.992	1.078	1.260	1.309	1.434
35°	1.162	1.184	1.233	1.379	1.425	1.565
40°	1.337	1.309	1.380	1.688	1.755	1.964

The values of temperature cœfficient between different temperatures have been calculated and they are given in the following table:

TABLE VIII

| Temp. coeff. bet. temps. | Acetone | | | Ether | | |
	$a = 0.8604$	0.5736	0.2868	0.9583	0.4863	0.2448
30°–35°	1.128	1.193	1.144	1.094	1.089	1.091
35°–40°	1.150	1.105	1.119	1.224	1.231	1.225
30°–40°	1.298	1.319	1.280	1.340	1.341	1.370

It can be seen from the above table that the values of the temperature coefficient are almost constant within limits of experimental error and are practically independent of the initial concentration of ferric chloride. Also it will be seen in the case of ether that the temperature coefficient is a function of the temperatures between which it is calculated.

The low values of the temperature coefficient obtained in both the cases indicate that the photo-reduction of ferric chloride in presence of ether and acetone may be considered as a truly photochemical reaction.

The effect of wave-length

The effect of different wave-lengths was examined by studying the kinetics of the reaction in radiations filtered through the three filters described before. The results obtained are given in the following tables:

TABLE IX

Ferric Chloride and Acetone

$a = 0 \cdot 9870$; $b = 0 \cdot 2764$; $T = 35°$

t	Blue filter		Yellow filter		Red filter	
	$X \times 10^2$	$K \times 10^4$	$X \times 10^2$	$K \times 10^4$	$X \times 10^2$	$K \times 10^4$
60	0·92	1·535	0·72	1·190	0·63	1·074
120	1·80	1·535	1·42	1·190	1·25	1·055
180	2·67	1·522	2·08	1·177	1·86	1·049
240	3·55	1·526	2·75	1·180	2·47	1·055

TABLE X

Ferric Chloride and Ether

$a = 0 \cdot 9583$; $T = 35°$

t	Blue filter		Yellow filter		Red filter	
	$X \times 10^2$	$K \times 10^4$	$X \times 10^2$	$K \times 10^4$	$X \times 10^2$	$K \times 10^4$
60	0·99	1·727	0·81	1·420	0·69	1·190
120	1·96	1·727	1·60	1·401	1·36	1·190
180	2·89	1·702	2·38	1·407	2·02	1·190
240	3·84	1·708	3·16	1·401	2·66	1·180

It can be seen from the above tables that the effect of the wavelength of the incident radiations on the velocity constant is quite marked. This has been brought out in the following table which gives the values of the unimolecular constant, taken from the above tables:

TABLE XI

Filter	$K \times 10^4$ for	
	Acetone	Ether
Blue ..	1·530	1·716
Yellow ..	1·184	1·407
Red ..	1·058	1·188

TABLE XII

I	Acetone ($a = 0 \cdot 972$)		Ether ($a = 0 \cdot 9583$)	
	$X \times 10^3$	$K \times 10^4$	$X \times 10^3$	$K \times 10^4$
25·00	7·38	1·266	8·64	1·496
21·15	6·12	1·074	7·20	1·266
14·45	4·32	0·767	4·86	0·844

It will be seen that the values of the velocity constants in the three frequencies used decrease in the order blue > yellow > red, that is, the reaction takes place the most in blue light and the least in red. These results are as expected since the total energy of the absorbed light increases with the increase in the frequency of the exciting radiations.

The effect of intensity

The effect of the intensity of the incident light was examined by study-ing the reaction for one hour in composite light at 35°. The changes in the incident intensity were effected by changing the distance of the source of light from the reaction cell, thereby causing no change in the quality of the light. The results obtained are given in Table XII.

It will be seen that the effect of the intensity of the incident light is quite marked, the velocity constant is increased on increasing the intensity. The following table gives the ratios of the velocity constants and the correspond-ing ratios of the intensities, in which I_1, I_2 and I_3 are the intensities and K_1, K_2 and K_3 the corresponding values of the velocity constants:

TABLE XIII

		Acetone	Ether
$I_2/I_1 = 1\cdot46$	$K_2/K_1 =$	$1\cdot40$	$1\cdot50$
$I_3/I_2 = 1\cdot18$	$K_3/K_2 =$	$1\cdot18$	$1\cdot18$
$I_3/I_1 = 1\cdot73$	$K_3/K_1 =$	$1\cdot65$	$1\cdot77$

It can be seen from the above table that the rate of reaction is directly proportional to the intensity of the incident light, the slight deviations being within the limits of experimental error. As the amount of absorbed radia-tion is directly proportional to the incident intensity (cf. Dhar, " The Che-mical Action of Light"), these results show that the rate of reaction is direct-ly proportional to the absorbed energy.

Quantum efficiency measurements

The quantum efficiency with different concentrations of ferric chloride for different wave-lengths was measured by using the same filters as used in the study of the kinetics of the reaction. The time of exposure of the reac-tion mixtures was one hour for all the measuremants. The number of mole-cules changed during the period of exposure was calculated from the titration data and the number of quanta absorbed was determined from the measure-ment of the absorbed energy. The results obtained are given below:

TABLE XIV

Organic compound	a	Quantum efficiency at 35° for		
		4725 A.U.	5975 A.U.	6625 A.U.
Acetone	0·50	0·24	0·20	0·16
	0·10	0·38	0·30	0·24
	0·05	0·41	0·32	0·26
Ether	0·48	0·52	0·42	0·34
	0·12	0·76	0·61	0·49
	0·06	0·82	0·66	0·53

It will be seen from the above table that the values of the quantum yield in case of acetone are low, being in all cases less than 0·5; in ethereal solutions of ferric chloride, however, the yields are much higher. Further in will be seen that the quantum efficiency increases with dilution; the increase is fairly large on decreasing the concentration from 0·5 to 0·1 but is comparatively much less when it is decreased from 0·1 to 0·05. Also it can be seen that the values of the quantum yield decrease as the wave-length of the exciting radiation is increased. It is evident, therefore, that more molecules of ferric chloride are changed for every quantum of light absorbed, in light of a higher frequency that in that of a lower one.

The effect of temperature on the quantum yield was examined by determining the quantum yields at 30° and 40° in addition to those at 35°. The effect was studied only in blue light. The results obtained are given in the following table:

TABLE XV

Organic compound	a	Quantum efficiency for $\lambda = 4725$ A.U. at		
		30°	35°	40°
Acetone	0·50	0·22	0·24	0·29
	0·10	0·34	0·38	0·44
	0·05	0·37	0·41	0·48
Ether	0·48	0·47	0·52	0·64
	0·12	0·69	0·76	0·95
	0·06	0·74	0·82	1·02

It will be seen that the temperature has quite a marked effect on the quantum yield of the reaction. Also it can be seen that it is more marked for the same rise of temperature at a higher temperature. These results are analogous to those obtained in the study of the effect of temperature on

A3a

the velocity constant in case of ethereal solutions of ferric chloride. Such results have been obtained in many cases studied in this laboratory, but the only other case reported in the literature is the work of Kuhn (8). While studying the photo-decomposition of ammonia he obtained a 50 per cent. increase in the quantum yield for every 100 degree rise in temperature. He attributed this to the change in the kinetics of the reaction at higher temperatures.

Summary

1. The photo-reduction of ferric chloride in presence of aqueous acetone and anhydrous ether is a unimolecular reaction.

2. The temperature and the frequency of the exciting radiations have a marked effect on the velocity constant of the reaction.

3. The rate of reaction is directly proportional to the intensity of the incident light.

4. The quantum yield of the reaction increases with dilution of ferric chloride, the temperature and the frequency of the exciting radiations and is of the order of $0 \cdot 5$ for acetone and $1 \cdot 0$ for ether.

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