Extinction Coefficients of Mixtures of Uranyl Nitrate and Organic Acids in the Ultraviolet, as Experimental Evidence in Favour of the Formation of Unstable Intermediate Compounds.

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It is well known that almost all organic acids undergo photochemical decomposition in presence of uranyl salts. The general mechanism of this photo-chemical reaction is not yet definitely settled, and this investigation was undertaken with the object of elucidating this problem.

Victor Henri (*Compt. rend.*, 1914, **158**, 181) has already observed that the extinction coefficient of mixtures of oxalic acid and uranyl salts in aqueous solution for wave-lengths in the ultraviolet is greater than the sum of the extinction coefficients of these solutions for the same radiation taken separately. No systematic work, however, has been done in the subject, and no clear explanation of this phenomenon has been offered.

If we accept the theory that a change in colour is due to a change in the nature of the molecular species, then it is not difficult to obtain a simple and quantitative explanation of this exaltation in the value of the extinction coefficients. Let us assume for the sake of simplicity that one molecule of uranyl nitrate (U) may combine with one molecule of an organic acid (A) to give us one molecule of the intermediate complex (M). Then applying the law of mass action, if x be the concentration of the intermediate complex, and U_1 and A_1 the initial concentration of uranyl nitrate and of the organic acid respectively,

$$[U_1 - x_1] \quad [A_1 - x_1] = Kx_1 \tag{1}$$

At the same temperature the value of K should remain constant. Let E_U^λ, E_A^λ and E_M^λ be the molecular extinction coeffeients for wave-length λ of the uranyl salt, the organic acid, and the intermediate complex respectively. Then the observed extinction coefficient for the mixture

$$E_1^\lambda = E_U^\lambda \left[U_1 - x_1 \right] l + E_A^\lambda \left[A_1 - x_1 \right] l + E_M^\lambda \left[x_1 \right] l \quad (2)$$

where l is length of the solution through which light passes. For other dilutions,

$$E_2^\lambda = E_U^\lambda \left[U_2 - x_2 \right] l + E_A^\lambda \left[A_2 - x_2 \right] + E_M^\lambda \left[x_2 \right] l \quad (3)$$

$$\text{and} \left[U_2 - x_2 \right] \quad A_2 - x_2 \Big] = Kx_2 \quad (4)$$

The values E_1^λ and E_2^λ, E_U^λ, E_A^λ, $[U_1]$, $[U_2]$, $[A_1]$, $[A_2]$ and l are experimentally measured magnitudes.

There are thus four unknown quantities x_1, x_2, K, and E_M^λ, and four equations, and hence their values can be determined. For any other wave-length, λ', since the value of K always remains the same, x can be easily calculated from equation (1) and therefore from a single measurement of extinction coefficient of mixture and of the components separately, it is possible to calculate the value of $E_M^{\lambda'}$, as will be clear from the following equation.

$$E^{\lambda'} = E_U^{\lambda'} \left[U - x \right] + E_A^{\lambda'} \left[A - x \right] + E_M^{\lambda'} \left[x \right]$$

From the tables given in the paper it will be seen that the experimental data of extinction coefficients of mixtures in most cases can be quantitatively explained—

(1) on the basis of an equilibrium in solution between the uranyl salt and organic acid as reactants and an intermediate complex formed by the loose combination of one molecule of each of the reactants, and

(2) on the assumption of a definite value of molecular extinction coefficients for each wave-length for the intermediate complex so formed.

EXPERIMENTAL.

The uranyl nitrate and the acids were carefully purified in the laboratory, and the extinction coefficients were measured with the aid of rotating sector photometer of Adam Hilger in conjunction with their quartz spectrograph.

Though the photographic density of the two spectra in juxtaposition can be compared fairly accurately still the probability of error in the value of the extinction coefficients is certainly ± 7 %.

The length of the tube containing the solution was 2 cm. in all the cases.

TABLE I.

M/2000 *Uranyl nitrate* (U) *and Formic Acid* (A); $K=10$.

	$\text{Log}\frac{I_0}{I_t}$ for wave-length (λ)				Conc. of int. complex as calculated.
	2770	2600	2545	2507	
M/2000 U	·25	·55	·6	·7	......
M acid	...	·1	·2	·5	
M/2000 U + M acid mixture ...	·35	·90	1·05	...	$\cdot455 \times 10^{-3}$
E calc.	·34	·92	1·07	...	
M/5 acid	...	...	·05	·1	
M/2000 U + M/5 acid mixture ...	·30	·75	·85	1·2	$\cdot33 \times 10^{-3}$
E calc.	·32	·75	·85	1·3	
M/10 acid	..	...	...	·05	
M/2000 U + M/10 acid mixture	·30	·7	·75	1·05	$\cdot25 \times 10^{-3}$
E calc.	·30	·7	·75	1·05	
M/20 acid	...	...	...	...	
M/2000 U + M/20 acid mixture	·25	·65	·7	·9	$\cdot165 \times 10^{-3}$
E calc.	·28	·65	·7	·9	
M/50 acid	...	...	...	...	
M/2000 U + M/50 acid mixture	·25	·6	·65	·80	$\cdot083 \times 50^{-3}$
E calc.	·27	·6	·65	·80	

In calculating the values of E for the various mixtures K has been assumed to be 10 in all the cases and E_M^λ given the following values for various wave-lengths—

λ	=	2770	2600	2545	2507
E_M	=	$\cdot 10 \times 10^3$	$\cdot 30 \times 10^3$	$\cdot 30 \times 10^3$	$\cdot 60 \times 10^3$

With M/1000 conc. of uranyl nitrate and varying conc. of formic acid, extinction coefficients could be measured for higher wave-lengths and the observed values of extinction coefficients for mixtures could be reproduced by assuming $K=10$ and

λ	=	2961	2770	2600
E_M	=	$\cdot 06 \times 10^3$	$\cdot 10 \times 10^3$	$\cdot 30 \times 10^3$

TABLE II.

M/2000 *Uranyl nitrate* (U) *and Acetic acid* (A); $K=6$.

	$\text{Log.}\frac{I_o}{I_t}$ for wave-length (λ)				Conc. of int. complex (x) as calculated.
	2770	2722	2600	2545	
M/2000 U ...	·25	·3	·55	·6	
4M acid ...	·1	·2	·3	·4	
Mixture ...	·75	1·0	1·45	...	$\cdot 48 \times 10^{-3}$
E calc. ...	·74	1·01	1·45	...	
M acid ...	...	...	·1	·1	
Mixture ...	·6	·75	1·2	1·40	$\cdot 429 \times 10^{-3}$
E calc. ...	·6	·75	1·19	1·39	
M/2 acid ...	...	...	...	·05	
Mixture ...	·55	·7	1·0	1·25	$\cdot 375 \times 10^{-3}$
E calc. ...	·56	·7	1·02	1·25	
M/10 acid ...	...	...	...	...	
Mixture ...	·4	·5	·80	·9	$\cdot 188 \times 10^{-3}$
E calc. ...	·4	·5	·79	·9	
M/50 acid ...	...	...	...	...	
Mixture ...	·3	·35	·60	·70	$\cdot 053 \times 10^{-3}$
E calc. ...	·29	·35	·62	·68	

In calculating the values of E^{λ} for the various mixtures K has been assumed to be 6 in all the cases and E^{λ}_{M} given the following values for various wave-lengths—

λ	=	2770	2722	2600	2545
E_M	=	$\cdot 41 \times 10^3$	$\cdot 53 \times 10^3$	$\cdot 63 \times 10^3$	$\cdot 60 \times 10^3$

With M/1000 conc. of uranyl nitrate and varying conc. of acetic acid, extinction coefficients could be measured for higher wave-lengths and the observed values of extinction coeff. could be reproduced by assuming $K=6$ and

λ	=	2961	2770	2722	2600
E_M	=	20×10^3	$\cdot 40 \times 10^3$	$\cdot 54 \times 10^3$	$\cdot 64 \times 10^3$

TABLE III.

M/2000 *Uranyl nitrate* (U) *and Propionic Acid* (A); $K=4$.

	$\log \frac{I_0}{I_t}$ for wave-length (λ)				x calculated.
	2770	2600	2545	2507	
M/2000 U ...	·25	·55	·6	·7	
M/5 acid ...	...	...	·1	·15	
Mixture ...	·55	1·10	1·25	...	$\cdot 22 \times 10^{-3}$
E calc. ...	·54	1·11	1·26	...	
M/10 acid ...	...	...	·05	·1	
Mixture ...	·45	·90	1·00	1·2	$\cdot 143 \times 10^{-3}$
E calc. ...	·44	·91	1·01	1·2	
M/20 acid ...	...	...	...	...	
Mixture ...	·35	·75	·80	·95	$\cdot 083 \times 10^{-3}$
E calc. ...	·35	·76	·81	·93	
M/50 acid ...	...	...	...	...	
Mixture ...	·3	·65	·70	·8	$\cdot 038 \times 10^{-3}$
E calc. ...	·3	·64	·69	·8	
M/100 acid ...	...	...	...	...	
Mixture ...	·25	·6	·65	·75	$\cdot 019 \times 10^{-3}$
E calc. ...	·27	·6	·65	·75	

In calculating the values of E, K has been assumed to be 4 and the following values of E_M^λ given—

λ	=	2770	2600	2545	2507
E_M	=	$\cdot 66 \times 10^3$	$1 \cdot 26 \times 10^3$	$1 \cdot 26 \times 10^3$	$1 \cdot 39 \times 10^3$

With M/1000 conc. of uranyl nitrate and different conc. of propionic acid, extinction coefficients could be measured for higher wave-lengths and the observed values of E could be reproduced by assuming $K=4$ and

λ	=	2961	2770	2600
E_M	=	$\cdot 34 \times 10^3$	$\cdot 66 \times 10^3$	$1 \cdot 23 \times 10^3$

TABLE IV.

M/2000 *Uranyl nitrate* (U) *and Oxalic acid* (A); $K=115$.

	$\text{Log}\frac{I_o}{I_t}$ for wave-length (λ):			x calculated.
	3364	3274	2961	
M/2000 U ...	...	...	·15	
M/10 acid ...	...	·1	·6	
Mixture ...	·25	·6	...	$\cdot 460 \times 10^{-3}$
E calc. ...	·24	·6	...	
M/20 acid ...	...	·05	0·3	
Mixture ...	·25	·55	1·40	$\cdot 426 \times 10^{-3}$
E calc. ...	·22	·52	1·37	
M/40 acid ...	...	...	·15	
Mixture ..	·20	·4	1·1	$\cdot 371 \times 10^{-3}$
E calc. ...	·19	·4	1·1	
M/100 acid ...	...	...	...	
Mixture ...	·15	·3	·75	$\cdot 266 \times 10^{-3}$
E calc. ...	·14	·3	·73	
M/200 acid ...	...	...	...	
Mixture ...	·1	·2	·55	$\cdot 182 \times 10^{-3}$
E calc. ...	·1	·2	·55	

In calculating the values of E, K has been assumed to be 115 in all the cases and the following values E_M^λ given—

λ	=	3364	3274	2961
E_M	=	·27 × 10³	·55 × 10³	1·08 × 10³

With M/1000 conc. of U and different conc. of oxalic acid E could be measured for higher wave-lengths with $K=115$ and

λ	=	3435	3364	3274	2961
E_M	=	·145 × 10³	·27 × 10³	·55 × 10³	1·08 × 10³

TABLE V.

M/2000 *Uranyl nitrate* (U) *and Malonic acid* (A); $K=80$.

	$\text{Log}\frac{I_o}{I_t}$ FOR WAVE-LENGTH (λ).				x calculated.
	2961	2770	2722	2600	
M/2000 U ...	·15	·25	·3	·55	
M/10 acid ...	...	...	...	...	
Mixture ...	·35	·85	1·1	...	·44 × 10⁻³
E calc. ...	·36	·86	1·1	...	
M/20 acid ...	...	...	...	...	
Mixture ...	·35	·8	1·0	...	·4 × 10⁻³
E calc. ...	·34	·8	1·0	...	
M/40 acid ...	...	...	...	...	
Mixture ...	·30	·70	·9	...	·33 × 10⁻³
E calc. ...	·31	·71	·9	...	
M/100 acid ...	...	...	...	...	
Mixture ...	·25	·55	·7	1·25	·22 × 10⁻³
Ecalc. ...	·26	·56	·7	1·25	
M/200 acid ...	...	...	...	...	·143 × 10⁻³
Mixture ...	·20	·45	·55	1·0	
E calc. ...	·21	·45	·55	1·0	

In calculating the values of E, K has been assumed to be 80 in all the cases, and the following values of E_M^λ for various wave-lengths given—

λ	=	2961	2770	2722	2600
E_M	=	·24 × 10^3	·69 × 10^3	·90 × 10^3	1·60 × 10^3

With M/1000 conc. of U and different conc. of malonic acid the following value of E_M^λ reproduced extinction coefficients for various mixtures with $K = 80$.

λ	=	3274	2961	2770
E_M	=	·12 × 10^3	·22 × 10^3	·69 × 10^3

TABLE VI

M/2000 *Uranyl nitrate* (U) *and Succinic acid* (A) ; $K = 50$

	$\text{Log}\frac{I_o}{I_t}$ FOR WAVE-LENGTH (λ)				x calculated.
	2770	2600	2545	2507	
M/2000 U ...	·25	·55	·6	·7	
M/10 acid ...	...	...	·05	·1	
Mixture ...	·50	1·00	1·1	1·4	·416 × 10^{-3}
E calc. ...	·47	·97	1·07	1·4	
M/20 acid ...	...	...	...	·05	
Mixture ...	·46	·90	·95	1·25	·357 × 10^{-3}
E calc. ...	·44	·91	·96	1·23	
M/40 acid ...	...		...	...	
Mixture ...	·40	·85	·90	1·1	·277 × 10^{-3}
E calc. ...	·39	·83	·88	1·1	
M/100 acid ...	...	...	...	...	
Mixture ...	·35	·70	·75	·95	·166 × 10^{-3}
E calc. ...	·34	·72	·77	·94	
M/200 acid ...	...	...	...	...	
Mixture ...	·3	·65	·7	·85	·100 × 10^{-3}
E calc. ...	·3	·65	·7	·84	

In calculating the values of E, K has been assumed to be 50 and the following values of E_M^λ given—

λ =	2770	2600	2545	2507
E_M =	$\cdot 28 \times 10^3$	$\cdot 53 \times 10^3$	$\cdot 53 \times 10^3$	$\cdot 75 \times 10^3$

With M/1000 conc. of U and different concentrations of succinic acid E could be measured for higher wave lengths with $K=50$ and

λ =	3274	2961	2770	2600
E_M =	$\cdot 18 \times 10^3$	$\cdot 21 \times 10^3$	$\cdot 30 \times 10^3$	$\cdot 53 \times 10^3$

Table VII.

M/2000 *Uranyl nitrate* (U) *and Glycollic acid* (A); $K=15$.

	$\text{Log}\frac{I_o}{I_t}$ for wave-length (λ).				x calculated.
	2770	2722	2600	2545	
M/2000 U ...	·25	·3	·55	·6	
M/5 acid ...	·3	·3	·3	·35	
Mixture ...	·85	1·1	1·45	...	$\cdot 375 \times 10^{-3}$
E calc. ...	·85	1·1	1·46	...	
M/20 acid ...	·05	·05	·05	·1	
Mixture ...	·45	·65	·95	1·2	$\cdot 214 \times 10^{-3}$
E calc. ...	·44	·64	·95	1·2	
M/50 acid ...	...	...	...	...	
Mixture ...	·35	·45	·75	·90	$\cdot 115 \times 10^{-3}$
E calc. ...	·34	·45	·74	·86	
M/100 acid ...	...	...	...	...	
Mixture ...	·3	·40	·65	·75	$\cdot 065 \times 10^{-3}$
E calc. ...	·3	·39	·65	·75	
M/200 acid ...	...	...	...	...	
Mixture ...	·25	·35	·60	·70	$\cdot 035 \times 10^{-3}$
E calc. ...	·28	35	·61	·68	

In calculating the values of E, K has been assumed to be 15 and the following values of E^{λ}_{M} given—

λ =	2770	2722	2600	2545
E_M	$\cdot 41 \times 10^3$	$\cdot 67 \times 10^3$	$\cdot 82 \times 10^3$	$1 \cdot 15 \times 10^3$

With M/1000 conc. of U and various conc. of glycollic acid E could be measured for higher wave-lengths with $K = 15$ and

λ =	3274	2961	2770	2722	2600
E_M =	$\cdot 13 \times 10^3$	$\cdot 17 \times 10^3$	$\cdot 40 \times 10^3$	$\cdot 63 \times 10^3$	$\cdot 82 \times 10^3$,

TABLE VIII.

M/2000 *Uranyl nitrate* (U) *and Lactic acid* (A); $K = 10$

	Log $\frac{I_0}{I_t}$ for wave-length (λ).				x calculated.
	2961	2770	2600	2545	
M/2000 U ...	·15	·25	·55	·6	
M acid ...	...	·2	·4	·5	
Mixture ...	·40	1·0	...	...	$\cdot 455 \times 10^{-2}$
E calc. ...	·42	1·0	...	...	
M/5 acid ...	...	...	·05	·1	
Mixture ...	·35	·65	1·25	1·5	$\cdot 380 \times 10^{-2}$
E calc. ...	·35	·65	1·26	1·5	
M/10 acid ...	...	...	...	·05	
Mixture ...	·3	·55	1·05	1·25	$\cdot 250 \times 10^{-2}$
E calc. ...	·3	·55	1·05	1·25	
M/20 acid ...	...	...	...	...	
Mixture ...	·25	·45	·90	1·0	$\cdot 165 \times 10^{-2}$
E calc. ...	·25	·45	·88	1·0	
M/50 acid ...	...	...	...	...	
Mixture ...	·2	·35	·70	·8	$\cdot 083 \times 10^{-2}$
E calc. ...	·2	·35	·71	·8	

In calculating the values of E, K has been assumed to be 10 and the following values of E_M^λ given—

λ =	2961	2770	2600	2545
E_M	·30 × 10^3	·60 × 10^3	1·00 × 10^3	1·20 × 10^3.

With M/1000 conc. of U and different conc. of lactic acid E could be measured for higher wave-lengths with K = 10 and

λ =	3274	2961	2770
E_M =	·21 × 10^3	·30 × 10^3	·60 × 10^3

TABLE IX.

M/2000 *Uranyl nitrate* (U) *and Tartaric acid* (A); K = 20.

	$\log \frac{I_0}{I_t}$ for wave-length (λ).				x calculated.
	2961	2770	2600	2545	
M/2000 U ...	·15	·25	·55	·6	
M/10 acid ...	...	...	·1	·1	
Mixture ...	·45	·65	1·45	...	·33 × 10^{-3}
E calc. ...	·45	·64	1·44	...	
M/20 acid ...	...	...	·05	·05	
Mixture ...	·35	·55	1·20	1·45	·25 × 10^{-3}
E calc ...	·37	·54	1·19	1·45	
M/40 acid ...	...	...	...	...	
Mixture ...	·3	·45	·95	1·15	·165 × 10^{-3}
E calc ...	·3	·44	·94	1·13	
M/100 acid ...	...	...	...	...	
Mixture ...	·20	·35	·75	·85	·083 × 10^{-3}
E calc. ...	·22	·35	·75	·87	
M/200 acid ...	...	...	...	...	
Mixture ...	·20	·3	·65	·75	·045 × 10^{-3}
E calc. ...	·19	·3	·65	·75	

In calculating the values of E, *K* has been assumed to be 20 and the following values of E^{λ}_{M} given—

λ	=	2961	2770	2600	2545
E_M	=	$\cdot 44 \times 10^3$	$\cdot 58 \times 10^3$	$1 \cdot 18 \times 10^3$	$1 \cdot 60 \times 10^3$

With M/1000 conc. of U and different conc. of tartaric acid E could be measured for higher wave-lengths with $K=20$ and

λ	=	3364	3274	2961	2770
E_M	=	$\cdot 30 \times 10^3$	$\cdot 45 \times 10^3$	$\cdot 45 \times 10^3$	$\cdot 60 \times 10^3$

TABLE X.

M/2000 *Uranyl nitrate* (U) *and Mandelic acid* (A); $K=50$.

	$\text{Log} \frac{I_0}{I_t}$ for wave-length (λ).				Conc. of int. complex as calculated.
	3274	2961	2770	2722	
M/2000 U ...	...	·15	·25	·3	......
M/10 acid ...	...	...	·4	...	
Mixture ...	·25	·55	1·25	...	$\cdot 415 \times 10^{-3}$
E calc. ...	·25	·55	1·25	...	
M/20 acid ...	...	...	·2	1·5	
Mixture ...	·20	·50	·95	...	$\cdot 357 \times 10^{-3}$
E calc. ...	·21	·49	·96	...	
M/50 acid ...	...	...	·05	·6	
Mixture ...	·15	·40	·65	...	$\cdot 25 \times 10^{-3}$
E calc. ...	·15	·39	·66	...	
M/100 acid ...	...	...	...	·8	
Mixture ...	·1	·3	·5	1·00	$\cdot 165 \times 10^{-3}$
E calc. ...	·1	·3	·5	·98	
M/200 acid ...	...	...	...	·15	
Mixture ...	...	·25	·40	·65	$\cdot 10 \times 10^{-3}$
E calc. ...	...	·24	·39	·68	

In calculating the values of E for the various mixtures, K has been assumed to be 50 in all the cases, and E_M^λ given the following values for various wave-lengths—

λ	=	3274	2961	2770	2722
E_M	=	$\cdot 30 \times 10^3$	$\cdot 48 \times 10^3$	$\cdot 72 \times 10^3$	$1 \cdot 15 \times 10^3$

With M/1000 conc. of uranyl nitrate and varying conc. of mandelic acid, extinction coeff. could be measured for higher wave-lengths and the observed values of extinction coeffs. for mixtures could be reproduced by assuming $K=50$ and

λ	=	3435	3364	3274	2961	2770
E_M	=	$\cdot 15 \times 10^3$	$\cdot 24 \times 10^3$	$\cdot 30 \times 10^3$	$\cdot 48 \times 10^3$	$\cdot 71 \times 10^3$

Certain regularities have been found between the values of dissociation constant (*K*) of intermediate complex formed by the combination of uranyl nitrate and organic acid and the constitution of that acid:

1. In a homologous series the value of *K* diminishes as we go higher up the series in a definite ratio for each addition of a (CH_2) group—

$$\frac{\text{Formic}}{\text{Acetic}} = \frac{10}{6} = 1 \cdot 66\,; \quad \frac{\text{Acetic}}{\text{Propionic}} = \frac{6}{4} = 1 \cdot 5\,;$$

$$\frac{\text{Oxalic}}{\text{Malonic}} = \frac{115}{80} = 1 \cdot 45\,; \quad \frac{\text{Malonic}}{\text{Succinic}} = \frac{80}{50} = 1 \cdot 6.$$

2. The value of *K* increases about 12 times as the hydrogen atom of a (CH_3) group is replaced by a (COOH) group—

$$\frac{\text{Oxalic}}{\text{Formic}} = \frac{115}{10} = 11 \cdot 5\,; \quad \frac{\text{Malonic}}{\text{Acetic}} = \frac{80}{6} = 13 \cdot 3\,; \quad \frac{\text{Succinic}}{\text{Propionic}} = \frac{50}{4} = 12 \cdot 5.$$

3. In the case of monobasic acids, replacement of a hydrogen atom in a (CH_3) group by (OH) group increases the value of dissociation constant 2·5 times.

$$\frac{\text{Glycollic}}{\text{Acetic}} = \frac{15}{6} = 2 \cdot 5\,; \quad \frac{\text{Lactic}}{\text{Propionic}} = \frac{10}{4} = 2 \cdot 5.$$

Investigations on the behaviour of aromatic acids in presence of uranyl nitrate could not be carried out as these aromatic acids are sparingly soluble in water and their extinction coefficients in near ultraviolet have very large values.

Investigations are in progress with a view to find out by this method if the photochemical oxidation of organic acids by ferric salts is preceded by the formation of an intermediate compound.

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