

## Some $\Delta\epsilon$ -Curves for Dissociations of Tropolones and Salts of Organic Bases

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In order to explore the applicability of the  $\Delta\epsilon$ -method to ionisable compounds other than phenols, the  $\Delta\epsilon$ -curves have been determined for a series of simple tropolones, arylamines and heterocyclic bases. It is shown that the  $\Delta\epsilon$ -method should be useful for the characterisation and estimation of these types of compounds.

The analytical value of the changes in light absorption which take place when chromophores undergo certain reactions, such as substitutions, hydrogenation, ionisation and complex formation, has been pointed out earlier<sup>1</sup>. The changes on ionisation have been used in the so-called " $\Delta\epsilon$ -method" worked out in these laboratories primarily for the study of the nature and frequency of the phenolic groups in lignin. With phenols this reaction causes a characteristic, not too small absorption change in the easily accessible ultra-violet region. To our knowledge, ionisation  $\Delta\epsilon$ -studies have so far been carried out mainly with phenolic materials (lignin, tanning agents *etc.*), and a reasonable number of model  $\Delta\epsilon$ -curves relating to the ionisation of phenols is now available in the literature (*cf.* Refs.<sup>2,3</sup> and references given therein). However, some further types of ionisation have also been studied. The work by Goldschmid referred to in Ref.<sup>3</sup> includes  $\Delta\epsilon$ -studies of the addition of a proton to CO-groups<sup>4</sup>. Investigations of a similar type have also been reported for some heterocyclic bases<sup>5</sup>.

An examination of other types of ionisable compounds was of interest as part of an investigation into the applicability of the  $\Delta\epsilon$ -method to other classes of natural and technical products. The present study includes some tropolones and a series of simple aromatic and heterocyclic bases.

### MATERIALS, SOLVENTS AND MEASUREMENTS

The compounds investigated are listed in Table 1 together with brief data on their purification and properties.

Table 1.

Compound	Solvent	UV absorption maxima				Cf. Ref.
		$m\mu$	loge	$m\mu$	loge	
I. Tropolone, prepd. from Ba salt *, distd. <i>in vacuo</i> , recryst. from heptane, m.p. 49—49.5°	95 % EtOH, 0.01 N in HCl	228	4.37	319	3.86	6
		351	3.77	366	3.70	
	95 % EtOH, N in KOH	240	4.37	263	3.85	
		334	4.10	398	4.07	
II. $\alpha$ -Thujaplicin ( $\alpha$ -isopropyl-tropolone), distd. <i>in vacuo</i> , recryst. from heptane, m.p. 33—34°	95 % EtOH, 0.01 N in HCl	239—40	4.46	318	3.82	7
		354—5	3.78	367	3.76	
	95 % EtOH, N in KOH	247	4.39	336—7	4.10	
		402—3	4.10			
III. $\beta$ -Thujaplicin ( $\beta$ -isopropyl-tropolone, hinokitiol), distd. <i>in vacuo</i> , recryst. from heptane, m.p. 50.5—51°	95 % EtOH, 0.01 N in HCl	239—40	4.49	320—1	3.82	7
		349	3.81			
	95 % EtOH, N in KOH	244—5	4.44	266	3.96	
		334—5	4.09	393	4.09	
IV. $\gamma$ -Thujaplicin ( $\gamma$ -isopropyl-tropolone), recryst. from heptane, m.p. 79—79.5°	95 % EtOH, 0.01 N in HCl	233	4.40	321—2	3.97	7
	95 % EtOH, N in KOH	242—3	4.40	336	4.20	
V. Pyridine, anal. grade (contg. 0.07 % water)	0.1 N H <sub>2</sub> SO <sub>4</sub> pH 10 carbonate buffer soln.	403	4.05			8
		255	3.72			
		251	3.39	256	3.44	
		262	3.27			
VI. Quinoline, purif. <i>via</i> sulphate (m.p. 161.5—162.5°), distd., $n_D = 1.6251$	0.1 N H <sub>2</sub> SO <sub>4</sub> pH 10 carbon. buffer soln.	233	4.58	313	3.83	10
		224—5	4.48	276—7	3.53	
		299	3.50	312	3.50	
		227	4.65	265—6	3.28	
VII. Isoquinoline, purif. <i>via</i> sulphate (m.p. 207—209°), distd., $n_D = 1.6147$ , m.p. 25.5—26°	0.1 N H <sub>2</sub> SO <sub>4</sub> pH 10 carbon. buffer soln.	273	3.29	331	3.60	11
		259	3.51	268	3.53	
		277	3.40	306	3.38	
		319	3.48			
VIII. Aniline, anal. grade (contg. 0.31 % water), $n_D = 1.5841$ .	0.1 N H <sub>2</sub> SO <sub>4</sub> pH 10 carbon. buffer soln.	248	2.11	254	2.19	11
		259—60	2.05			
		230	3.90	280	3.13	
		259	2.40	266	2.29	
IX. <i>o</i> -Toluidine, purif. <i>via</i> oxalate (m.p. 160—160.5°), distd. <i>in vacuo</i> , $n_D = 1.5716$	0.1 N H <sub>2</sub> SO <sub>4</sub> pH 10 carbon. buffer soln.	230	3.89	280	3.25	14
X. <i>m</i> -Toluidine, anal. grade (contg. 0.16 % water), $n_D = 1.5669$	0.1 N H <sub>2</sub> SO <sub>4</sub> pH 10 carbon. buffer soln.	260—1	2.47	268	2.39	14
		232—3	3.88	281—2	3.16	
XI. <i>p</i> -Toluidine, purif. <i>via</i> oxalate (m.p. 163—169°), recryst. from water and dil. EtOH, m.p. 43—44°	0.1 N H <sub>2</sub> SO <sub>4</sub> pH 10 carbon. buffer soln.	260	2.35	268	2.24	14, 15
		233	3.88	286	3.12	
XII. 1-Naphthylamine, recryst. from dil. EtOH, m.p. 48—49°	0.1 N HCl	268	3.74	277	3.80	16
		285	3.62			
	pH 10 carbon. buffer soln.	236—7	4.36	304	3.70	
XIII. 2-Naphthylamine, recryst. from water and dil. EtOH, m.p. 110—110.5°	0.1 N HCl	220	4.93	266—7	3.65	16
		273—4	3.68			
	pH 10 carbon. buffer soln.	234	4.73	269	3.68	
		278	3.75	289	3.61	
		334—5	3.23		16	

\* Compound supplied by Dr. H. Fernholz.

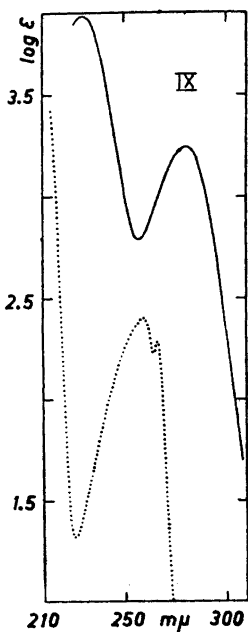


Fig. 1. Absorption curves for *o*-toluidine in 0.1 N  $\text{H}_2\text{SO}_4$  (.....) and in pH 10 carbonate buffer solution (—).

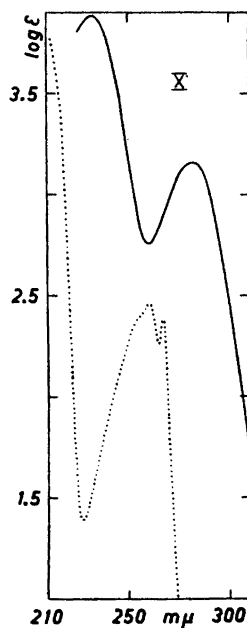


Fig. 2. Absorption curves for *m*-toluidine in 0.1 N  $\text{H}_2\text{SO}_4$  (.....) and in pH 10 carbonate buffer solution (—).

The ultra-violet absorption curves were determined for solutions of these substances in the acidic and alkaline solvents listed in the same table. The solvents were chosen so as to give a complete set of curves for the tropolones and the tropolonate ions in ethanol and for the bases and their ions in water.

A Beckman Model DU spectrophotometer with 1 cm calibrated silica cells was used for the measurements. The concentrations of the solutes were varied so as to keep  $\log(I_0/I)$  within the limits of 0.1 and 1.5. In critical regions readings were made at 1–2  $\text{m}\mu$  intervals, otherwise at every 5  $\text{m}\mu$ .

The difference curves were calculated by subtracting the  $\epsilon$ -values for the acidic solutions from the corresponding  $\epsilon$ -values for the alkaline solutions.

## RESULTS AND DISCUSSION

The absorption maxima found are listed in Table 1. The ultra-violet absorption curves for these compounds have already been studied in various solvents and reported in the literature. It is true that earlier data in many cases show great discrepancies, but for all compounds it was possible to find curves or figures in the literature (references in Table 1) which agree well with the results reported here.

The absorption curves are not reproduced except for the toluidines (Figs. 1–3) for which the literature does not give complete information.

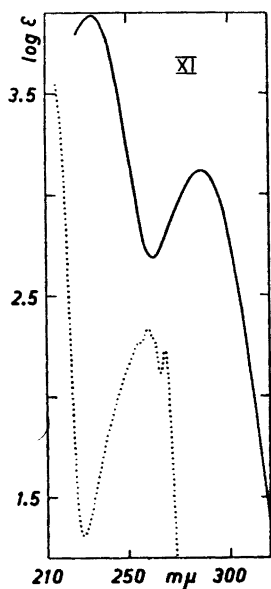


Fig. 3. Absorption curves for *p*-toluidine in 0.1 N  $\text{H}_2\text{SO}_4$  (.....) and in pH 10 carbonate buffer solution (—).

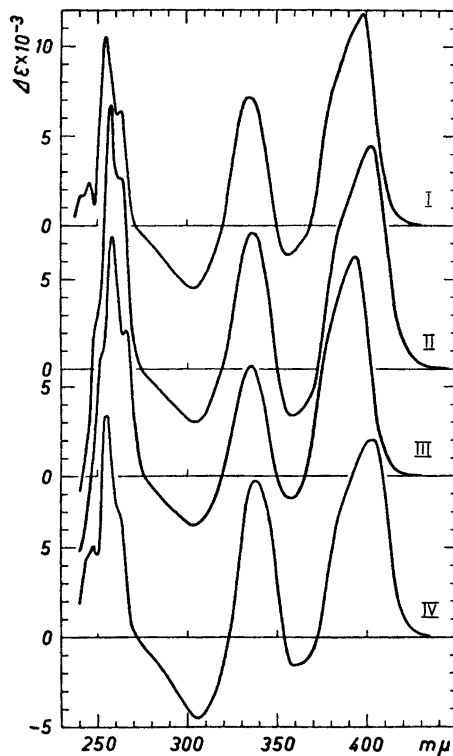


Fig. 4.  $\Delta \epsilon$ -curves for ionisation of tropolone (I),  $\alpha$ -thujaplicine (II),  $\beta$ -thujaplicine (III) and  $\gamma$ -thujaplicine (IV) in ethanol.

The ionisation difference curves for tropolone and its *C*-isopropyl derivatives are given in Fig. 4. Because of their similar electronic structures these compounds give closely related  $\Delta \epsilon$ -curves. The curves are quite characteristic and distinct from those of any phenols so far investigated. This type of  $\Delta \epsilon$ -curve is, of course, by no means characteristic of all tropolones. Changes such as the introduction of additional hydroxyl groups in the ring or ring-conjugated double bonds give rise to marked changes in the electronic structure and, hence, in the  $\Delta \epsilon$ -curve.

Fig. 5 gives the  $\Delta \epsilon$ -curves for the conversion of the pyridinium, quinolinium and isoquinolinium ions into the corresponding bases. Like most carboxylic acids these heterocyclic ammonium ions show a hypsochromic shift, hence a long-wave  $\Delta \epsilon$ -minimum on loss of a proton (*cf.* Ref.<sup>3</sup>).

Due to the spectrochemically similar electronic structures of the arylamines and the phenolate ions and of the arylammonium ions and the phenols, the conversion of anilinium ion and the toluidinium ions into the bases gives  $\Delta \epsilon$ -curves (Fig. 6) which are similar to the ionisation  $\Delta \epsilon$ -curves for the corre-

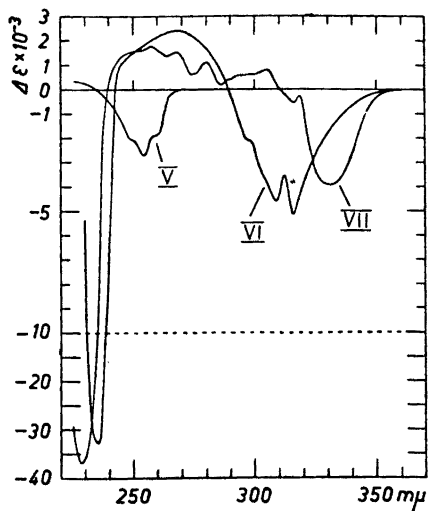


Fig. 5.  $\Delta\epsilon$ -curves for loss of a proton from the pyridinium (V), quinolinium (VI) and isoquinolinium (VII) ions in aqueous solutions.

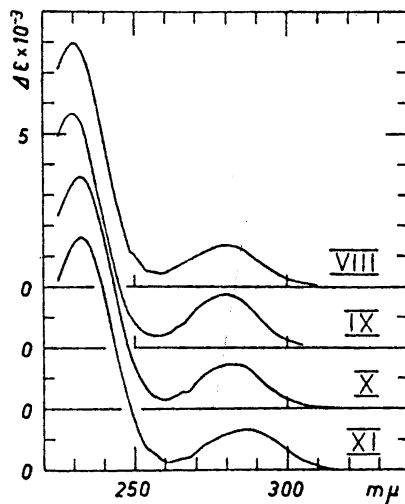


Fig. 6.  $\Delta\epsilon$ -curves for loss of a proton from the anilinium (VIII), *o*-toluidinium (IX), *m*-toluidinium (X) and *p*-toluidinium (XI) ions in aqueous solutions.

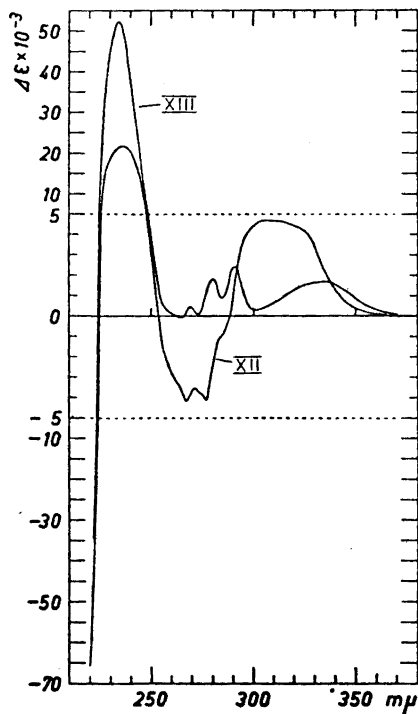


Fig. 7.  $\Delta\epsilon$ -curves for loss of a proton from the  $\alpha$ -naphthylammonium (XII) and  $\beta$ -naphthylammonium (XIII) ions in aqueous solutions.

Table 2. Ionisation of tropolones (95 % EtOH, 0.01 N in HCl  $\rightarrow$  95 % EtOH, N in KOH)

Compound	$\Delta\varepsilon$ -maxima				$\Delta\varepsilon$ -minima			
	m $\mu$	$\Delta\varepsilon$	m $\mu$	$\Delta\varepsilon$	m $\mu$	$\Delta\varepsilon$	m $\mu$	$\Delta\varepsilon$
I	241	1 700	245	2 400	242	1 700	248	1 200
	254	10 600	263	6 400	261	6 200	303-4	-3 500
	334-5	7 200	398	11 800	356	-1 600		
II	257	14 800	263	10 700	262	10 700	304-5	-2 900
	336	7 600	402	12 500	358	-2 600		
III	258	13 400	266	8 200	264	7 900	304	-2 700
	335	6 200	393	12 300	357	-1 300		
IV	247-8	5 100	255	12 400	250	4 600	306	-4 500
	337-8	8 700	403	11 200	359	-1 600		

sponding phenols<sup>3</sup>. The similarity in  $\Delta\varepsilon$ -curves between the naphthyl-ammonium ions (Fig. 7) and the corresponding naphthols<sup>3</sup> is, however, less pronounced.

The maxima and minima of the difference curves just discussed are given in Tables 2 and 3. The accuracies of these  $\Delta\varepsilon$ -values were estimated approximately, assuming<sup>2</sup>  $e_{\varepsilon}/\varepsilon = 0.02$ . The  $\Delta\varepsilon$ -values were rounded off accordingly, so that errors will generally occur only in the last figure.

It follows from the results presented that all the simple tropolones and bases investigated give characteristic  $\Delta\varepsilon$ -curves. There is considerable similarity within groups of closely related compounds. The differences between different types of compounds are also marked. All of the substances, except perhaps pyridine, give reasonably high, sometimes very high,  $\Delta\varepsilon$ -values above 230 m $\mu$ . It should, therefore, be possible to characterise and estimate the above compounds by means of the  $\Delta\varepsilon$ -method.

Table 3. Conversion of amine salts into amines (0.1 N H<sub>2</sub>SO<sub>4</sub>  $\rightarrow$  pH 10 carbonate buffer solution)

Compound	$\Delta\varepsilon$ -maxima				$\Delta\varepsilon$ -minima			
	m $\mu$	$\Delta\varepsilon$	m $\mu$	$\Delta\varepsilon$	m $\mu$	$\Delta\varepsilon$	m $\mu$	$\Delta\varepsilon$
V	250	-2 100			249	-2 100	254	-2 700
VI	268-9	2 410	312	-3 600	236	-32 900	309	-4 600
					316	-5 200		
VII	257	1 770	269	1 500	228-9	-37 000	264	1 300
	280	1 110	305	800	274	590	286	200
	318	-300			316	-600	331-2	-3 940
VIII	230	8 000	280	1 350	259	440		
IX	230	7 700	280	1 770	257	370		
X	232-3	7 600	266	530	260-1	280	267	530
	231-2	1 440						
XI	233	7 600	286-7	1 320	261	280		
XII	237	21 700	271	-3 500	267	-4 100	277	-4 100
	305-6	4 700						
XIII	234	52 000	269	400	264	-100	273	100
	279-80	1 800	291	2 400	285	900	301	310
	334-5	1 680						

The  $\Delta\epsilon$ -method is particularly useful for the analysis of difficultly separable mixtures and for the structural elucidation of complex molecules containing two or more separate chromophores. It might for example be used to locate hydroxyl groups in the heterocyclic or in the phenyl moiety in alkaloids of the benzyl-isoquinoline and angostura types. There are also obvious applications in the fields of purines, pterines, nucleic acids<sup>5</sup> and proteins. In addition to the  $\Delta\epsilon$ -curve the pH region at which the absorption change occurs is also indicative of the ionisable chromophore. One of the chief advantages of the method is that only small amounts of material are needed.

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