IR SPECTROSCOPY OF THE PROTONATION PROCESS OF PHTHALIMIDE DERIVATIVES

By

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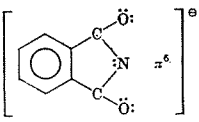
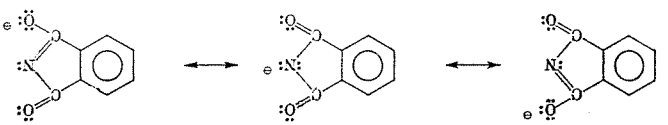
In this paper from among the phthalimides, N-phthalimides and N-phenil-phthalimides substituted in para position, the behaviour of chlorine, bromine and iodine derivatives depending on pH have been studied in aqueous-acetonic solutions.

Certain derivatives of the N-phenil-phthalimides are utilized as pestides. On the basis of their structure they can be assumed to have different stabilities in media of different pH values. It is important to clear up this problem from the point of view of the physiological effects of the above mentioned structures, depending on the stabilization of the anions of carboxylic acid, acid amides or the derivatives of the imide acids in an appropriate medium. It seemed advisable to follow the continuous structural changes by IR spectra recorded in a series of Britton—Robinson buffer solutions.

The phthalimides and the examined substituted N-phenil-phthalimides are analogous in structure to II. r. acid amides. [1] The structural formula of the anion of acid amides in an appropriate medium is as follows:



this can be described with the following structures:



In the protonation process the ring cleavage is presumably accompanied by the development of amide groups which can be characterized by the following structure:

(One of the hydrogen atoms may be substituted by alkyl or aryl.)

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In the IR spectra the bands of carbonyl groups have been studied on the basis of literature on IR spectroscopy of cyclic amides, of compounds containing carboxyl ion and of carboxylic acids [2—8].

Experimental

Aqueous-acetonic solutions of phthalimide, N-phenyl-phthalimide, p-chlorine-N-phenyl-phthalimide, p-bromine-N-phenyl-phthalimide and p-iodine-N-phenyl-phthalimide were prepared and solutions of different pH-values were produced with a series of the Britton-Robinson buffer solution. The solutions contained 1 mg/ml of the substance. The samples were synthetized in the laboratory for organic chemistry at Novi Sad. The pH values were measured with glass-electrodes.

Of these series of solutions IR spectra were recorded in a KRS 5 cell of 1 mm thickness by means of an IR spectrophotometer Type Zeiss UR-10, under the following experimental conditions:

Recording speed: 50 cm^{-1}/min
Slit program: 4
Time of total deflection: 50 sec
Spectrum scale: 12 mm/100 cm^{-1}
Amplification: 7
Band width: 2
Time constant: 2

Evaluation of results

The spectra obtained are seen in Figs 1 to 5. Although the spectral bands of solvents have been compensated the total band assignation of spectra has not been dealt with because of their strong absorption, only the changes occurring in the range of 800 to 2000 cm^{-1} were studied.

The structures presumed on the evaluation of spectra, and the observations supporting these structures are summarized in Table 1. In Table 2 the presumed pH dependent structures are summarized, indicating the intervals of their appearance in the case of our samples.

Evaluation of the spectra shows that in acidic media (ph < 3) ring cleaving is accompained by the formation of a $-COOH$ group. From pH $= 3$ the original (imide) structure is ring cleavage and $-COO^-$ ion, then for substituted the derivatives the ring is again closing at pH values slightly differing for each compound.

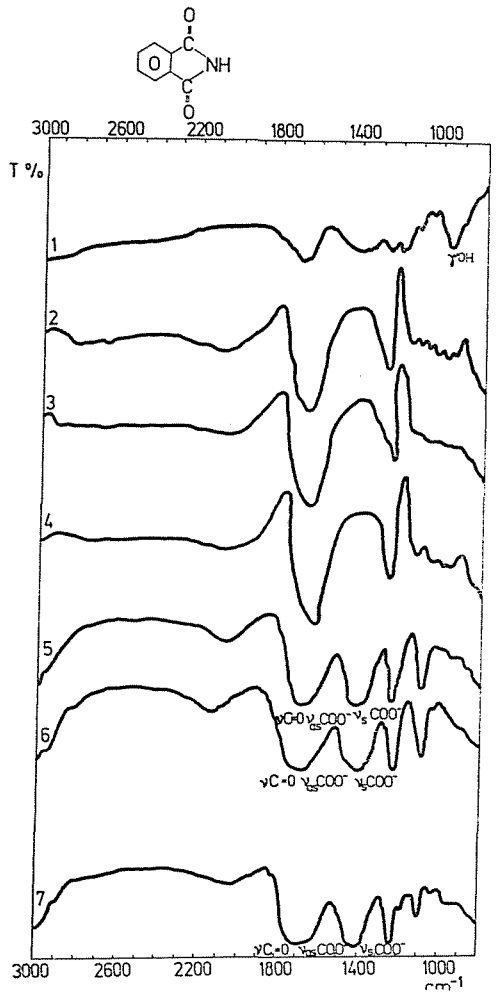


Fig. 1. IR spectra of phthalimides in aqueous-acetonic solutions*

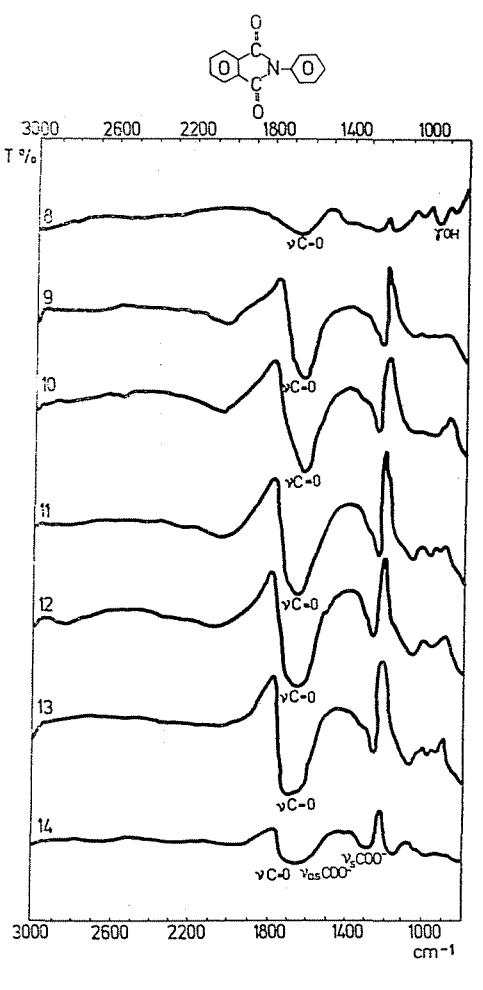


Fig. 2. IR spectra of phenyl-phthalimides in aqueous-acetonic solutions*

Subsequently we plan to use also other methods — first of all NMR spectroscopy — for the verification of the assumed structures.

The described examinations aimed at establishing the pH-ranges including components of identical properties. Results are seen in Table 2.

In addition to structures shown in the Table, other similar functional components may arise.

Our further investigations will also study these possibilities.

* ν: Stretching vibration; ν_s, ν_{as}: symmetrical and asymmetrical stretching vibration γ: bending vibration out of plane

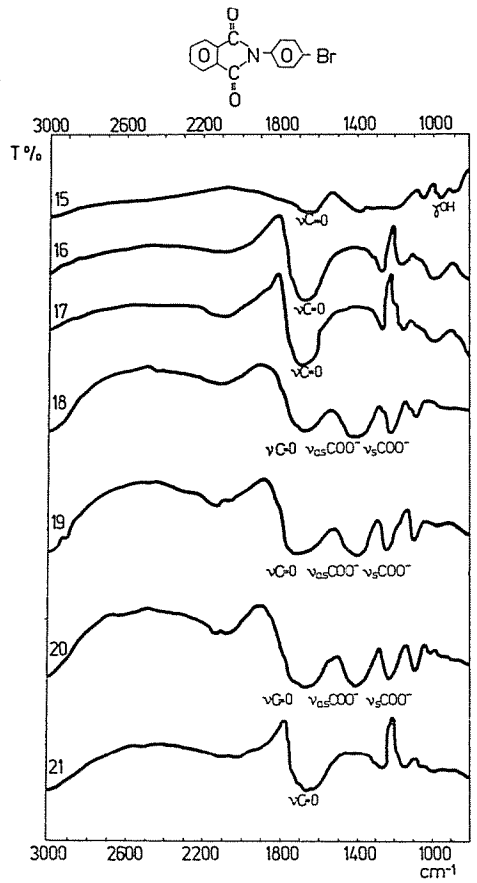


Fig. 3. IR spectra of p-bromine-phenyl-phthalimide in aqueous-acetonic solutions*

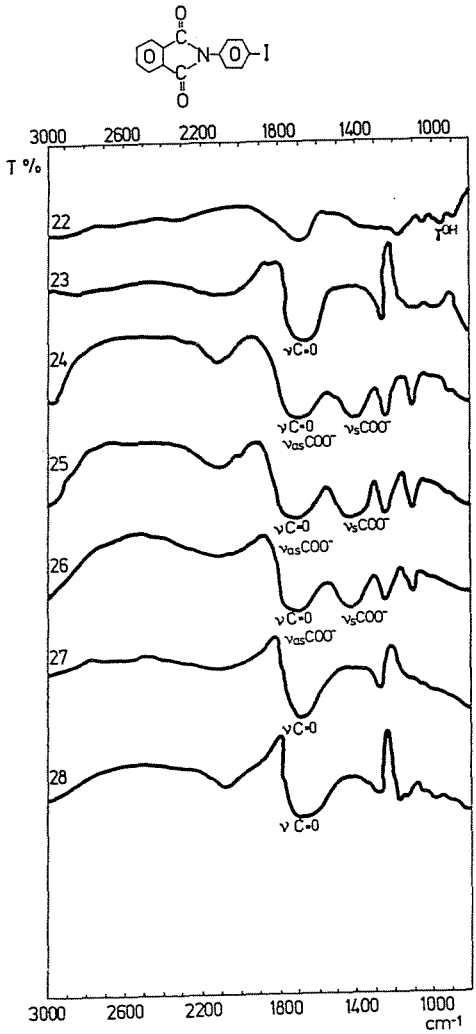


Fig. 4. IR spectra of p-iodine-phenyl-phthalimide in aqueous-acetonic solutions*

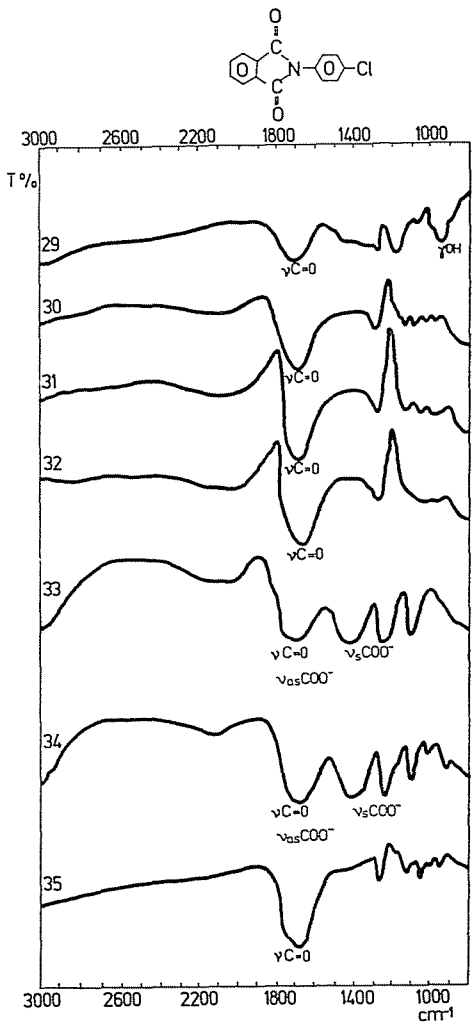


Fig. 5. IR spectra of p-chlorine-phthalimide in aqueous-acetonic solutions*

Table 1

Conclusion drawn from the IR spectra of substances

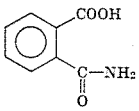
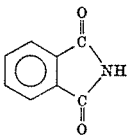
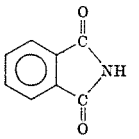
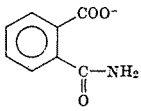
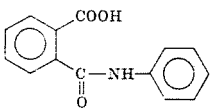
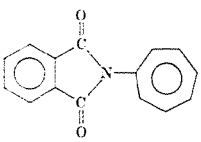
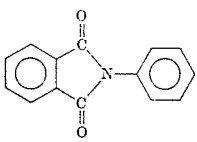
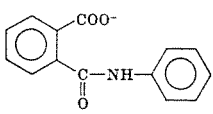
Substance examined	Sample No.	pH	Structure assumed	Explanation of assumption
	1	<0		The stretching vibration band (1700 cm^{-1}) of CO and the −OH banding vibration out of plane of −COOH group appear (900 cm^{-1})
	2 3 4	2.94 6.14 9.63		Solvents prevent spectral bands from showing the structure of spectra recorded in crystalline state. The two spectral bands originating from the coupled vibration of the two carbonyl groups are not separated but appear as an inflexion
Fig. 1	5 6 7	10.59 11.27 >14		The bands of $-COO^-$ ion appear in the spectra: the asymmetric stretching vibration merges with the amide I band (1700−1600 cm^{-1}), the symmetric stretching vibration appears at 1400 cm^{-1}
	8	<0		see Sample No. 1
	9 10 11 12 13	3.18 6.30 9.95 10.90 11.12		see Samples No 2, 3, 4
Fig. 2	14	>14		see Samples No 5, 6, 7

Table 1 (continued)

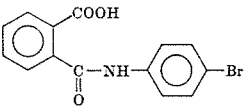
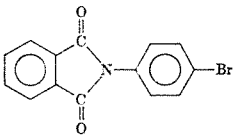
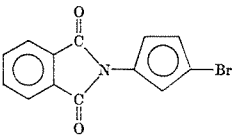
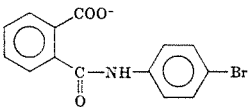
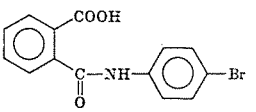
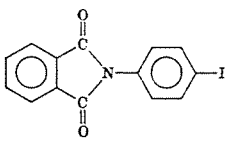
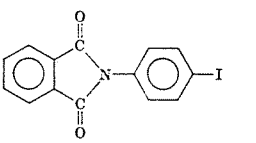
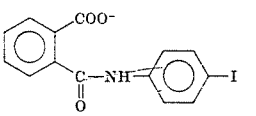
Substance examined	Sample No.	pH	Structure assumed	Explanation of assumption
	15	< 0		see Sample No. 1
	16 17	3.0 6.25		see Samples 2, 3, 4
	18 19 20	9.96 10.81 11.40		see Samples No. 5, 6, 7
Fig. 3	21	> 14	Ring is closed again	The bands of −COO ion disappear from the spectrum their becomes similar to that of imide form
	22	< 0		see Sample No. 1
	23	2.64		see Samples No. 2, 3, 4
	24 25 26	6.20 9.90 11.02		see Samples No. 5, 6, 7
Fig. 4	27 28	11.22 > 14	Ring is closed again	see Sample No. 21

Table 1 (continued)

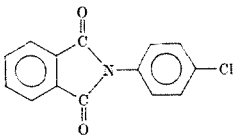
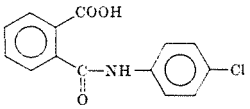
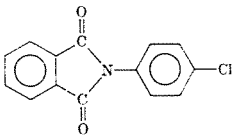
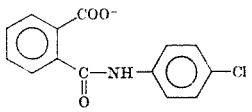
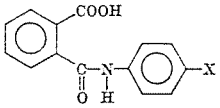
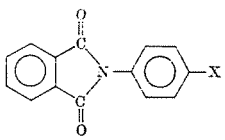
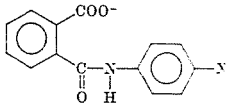
Substance examined	Sample No.	pH	Structure assumed	Explanation of assumption
 Fig. 5	29	<0		see Sample No. 1
	30	3.0		see Samples No. 2, 3, 4
	31	6.35		
	32	9.95		
	33	11.32		see Samples No. 5, 6, 7
	34	12.80		
	35	> 14	Ring is closed again	see Sample No. 21

Table 2

The structure of phthalimide, phenyl-phthalimide and p-halogen substituted phthalimide

Symbol	I	II	III
Structure			

Compound	Structure														
phthalimide	I						II						III		
phenyl-phthalimide	I						II						III		
p-iodine-phenyl-phthalimide	I						II		III				ring closure		
p-bromine-phenyl-phthalimide	I						II				III		ring closure		
p-chlor-phenyl-phthalimide	I						II				III		ring closure		
pH	5	4	3	2	1	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	14

Summary

Structure variations of phthalimide-, N-phenyl-phthalimide and chlorine-, bromine- and iodine-N-phenyl-phthalimides substituted in para-position have been studied pH, by IR spectrophotometry in aqueous-acetonic solutions.

The examinations have been carried out in Britton-Robinson buffer series structural variations lading itself to observe in the range pH = −5 to pH = 14.

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