SPECTRA OF SCHIFF BASES IN CONCENTRATED
SULPHURIC ACID AND IN SULPHURIC ACID/METHANOL

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The spectral behaviour of Schiff bases derived from salicylaldehyde and alkylenediamines or aromatic diamines has been studied spectrophotometrically in concentrated sulphuric acid and in sulphuric acid/methanol (18.3—2 mol/dm³ H_2SO_4). The first-order rate constants for cleavage of the alkylenediamine derivatives have been calculated. For the o-, m- and p-phenylenediamine derivatives two different phenomena can be observed.

The u.v. absorption spectra of azomethines in different solvents have been discussed in a large number of articles *e.g.* [1—5] and several authors have investigated the ionization and protonation of these bases and other organic compounds [6—8]. Relatively little attention has been paid to the behaviour of Schiff bases in strongly acidic media *e.g.* [9]. In the present communication the spectral properties of sixteen salicylaldimines in concentrated sulphuric acid and in sulphuric acid/methanol systems are reported. For an explanation of the symbols we refer to our earlier paper [10].

Experimental

The preparation of the Schiff bases was described previously [10]. The spectra were recorded between 200 and 600 nm on a SPECORD UV-VIS spectrophotometer at 293 ± 0.1 K, using 0.1, 1.0 and 10 cm quartz cells; the Schiff base concentrations of the solutions varied in the range $2.5—3.1 \cdot 10^{-4}$ mol/dm³. The solvent series were prepared by dilution of 98% sulphuric acid (Merck p.a.) with spectroscopically pure methanol; the acid concentrations were controlled analytically.

The spectra of the alkylenediamine derivatives and of BHSAL-pfda were run from 200 to 400 nm, at time intervals of 5, 10 or 20 min; the limiting curves were measured after 1440 min. The spectra of the o- and m-phenylenediamine derivatives were monitored within five min. after the dissolution; no significant change of the spectra can be observed after 2—20 min.

The first-order rate constant, k, may be calculated from the relation

$$k = \frac{2.303}{t} \log \frac{E_\infty - E_0}{E_\infty - E_t},$$ where E_t, E_0 and E_∞ are the absorbances at times t, $t=0$ and $t=\infty$, respectively. The rate constants were obtained from 4 to 5 determinations; the values were reproducible to within $\pm 5\%$.

Results and discussion

a) *The alkylenediamine derivatives.* The u.v. spectra of the Schiff bases studied show a very characteristic change with time; a set of curves is presented in Fig. 1; the calculated first-order rate constants are listed in Table I. From Fig. 1 it can be seen that three wellmarked isobestic points appear at around 210, 270 and 340 nm, which proves that there is no accumulation of intermediates between the base and the aldehyde resulting from its hydrolysis [e.g.11].

Table I

First-order rate constant measured in 18.30 mol/dm³ sulphuric acid

Compd.	$k \cdot 10^2$	Compd.	$k \cdot 10^2$
BHSAL-en	1.45	BHSAL-nmda	1.65
BHSAL-pda	1.29	BHSAL-dmda	3.84
BHSAL-bda	1.14	BHSAL-deta	2.28
BHSAL-pmda	1.00	BHSAL-teta	1.25
BHSAL-hxmda	2.69	THSAL-teta	0.12
BHSAL-hpmda	1.31	THSAL-tatea	0.57
BHSAL-omda	1.75		

The rate constants, k, decrease in the sequence $C_2 \rightarrow C_5$, which is in agreement with the finding of CHARETTE ET AL. [12]; the k values decrease as the basicity of the amines increases. In the case of longer alkyl chains (C_6—C_{10}) the rate constants show extremely high values for even C atom numbers. A reverse relationship between
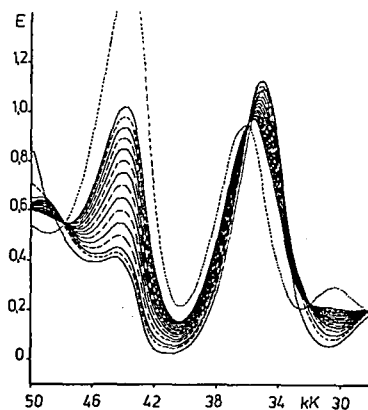

Fig. 1. Spectral changes of THSAL-teta in 18.30 mol/dm³ sulphuric acid; $d=$ $=0.1$ cm; T$=293$ K; concentration$=$ $=2.5 \cdot 10^{-3}$ mol/dm³. The curves were monitored at 20 min intervals. The limiting curve was measured after 1440 min
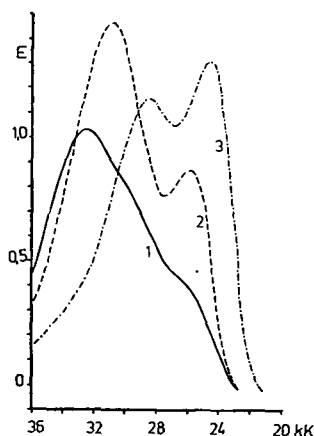
Fig. 2. Absorption spectra of 18.30 M sulphuric acid solutions of 1: BHSAL-ofda; 2: BHSAL-mfda; 3: BHSAL-pfda. Concentration$=3.14 \cdot 10^{-4}$ mol/dm³; d$=0.1$ cm

k and the basicity of the amines is found in the case of BHSAL-deta and BHSAL-teta (log $\beta_n=23.40$ and 29.11), while THSAL-tatea hydrolyzes about four times as rapidly as THSAL-teta.

From Fig. 1 it is seen that for THSAL-teta a high-intensity band develops at around 225—230 nm; the 290 nm band shows a blue shift and its intensity decreases. The limiting curve, measured after 24 hours, is almost identical to the theoretical curve resulting from the individual curves of the components.

b) *Phenylenediamine derivatives.* The methanolic solutions of the three bases studied show two characteristic bands in the spectral range 250—400 nm, with decreasing intensity in the sequence $o-m-p$. The position of the shorter-wavelength bands scarcely changes, but the second bands show a considerable red shift from o to p. These bands can be assigned to the $\pi \rightarrow \pi^*$ transition of the aromatic nucleus (Table II).

Table II

Spectral data on methanolic and sulphuric acid* solutions of the Schiff bases

Schiff base	Solvent		nm (log ε)		
BHSAL-pfda	MeOH	211(5.09)	~230	266(4.75)	332(4.57)
	H₂SO₄		~225	308(4.48)	~380
BHSAL-mfda	MeOH	216(4.61)	230(4.59)	273(4.52)	343(4.48)
	H₂SO₄		~240	323(4.66)	387(4.44)
BHSAL-pfda	MeOH	209(4.55)	~233	274(4.02)	366(4.31)
	H₂SO₄	~240	266(3.95)	350(4.57)	403(4.62)

* [H₂SO₄]=18.30 mol/dm³.

In concentrated sulphuric acid (~18 mol/dm³) a drastic spectral change can be observed (Table II, Fig. 2). BHSAL-ofda exhibits a band at 308 nm, with a shoulder at 380 nm, but the spectra of BHSAL-mfda and BHSAL-pfda show two bands at 323 and 387 nm, and at 350 and 403 nm, respectively, with a reversed intensity relation. It is probable that these spectra can be assigned to the totally protonated forms of the bases.

Depending on the acid concentrations, a set of curves may be measured in the sulphuric acid/methanol systems (Fig. 3). With decreasing acid concentration, the bands in the ranges 290—380 nm and 255—210 nm decrease and increase in intensity, respectively. Below about 9 mol/dm³ acid, a new band appears at 255 nm; the limiting curves, at about 4 mol/dm³ acid, correspond to the curves calculated from the methanolic spectra of the Schiff base components.

The curves at higher (>10 mol/dm³) and lower (<10 mol/dm³) acid concentrations give isobestic points at 265 and 230 nm, respectively. It is possible that in the former concentration range a gradual deprotonation takes place, and in the latter range a gradual disintegration of the Schiff bases; the various species form equilibrium systems. It must be noted that plots of the molar extinction coefficient ε_{292} against log $c_{H_2SO_4}$ are sigmoid curves (Fig. 4); the inflection points for o- and m-derivatives lie at 9.7 and 11.6 mol/dm³ acid, respectively (Table III).
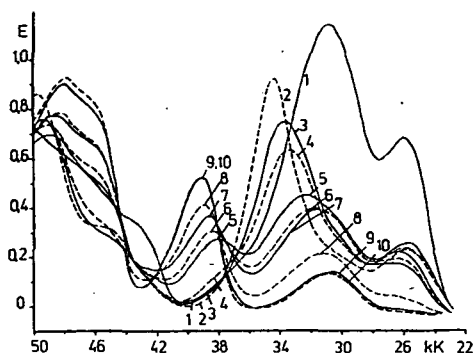
Fig. 3. Changes in spectra of BHSAL-mfda in sulphuric acid/methanol mixtures. $c_{H_2SO_4} = 1$: 18.30; 2: 17.40; 3: 13.95; 4: 11.83; 5: 9.75; 6: 9.06; 7: 8.36; 8: 6.96; 9: 5.57; 10: 4.16 mol/dm³. $c_{s.b.} = 2.5 \cdot 10^{-4}$ mol/dm³; d=0.1 cm
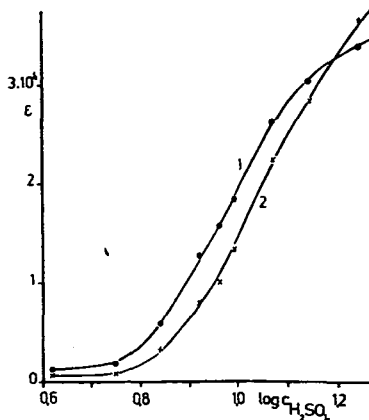

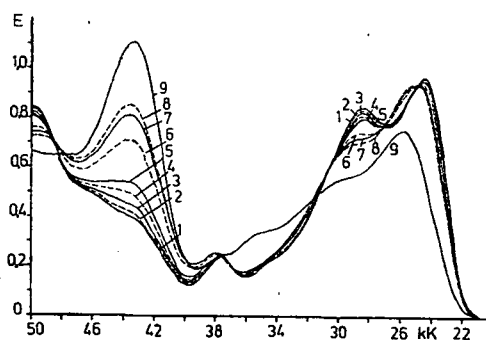*Fig. 4.* Plot of ε_{292} values vs. log $c_{H_2SO_4}$ for BHSAL-ofda (1) and BHSAL-mfda (2)

Fig. 5. Spectral changes of BHSAL-pfda with time: t=1: 1.5; 2: 20; 3: 45; 4: 75; 5: 105; 6: 240; 7: 360; 8: 420; 9: 1440 min. $c_{s.b.} = 2.5 \cdot 10^{-4}$; $c_{H_2SO_4} = 18.30$ mol/dm³; d=0.1 cm; T=293 K
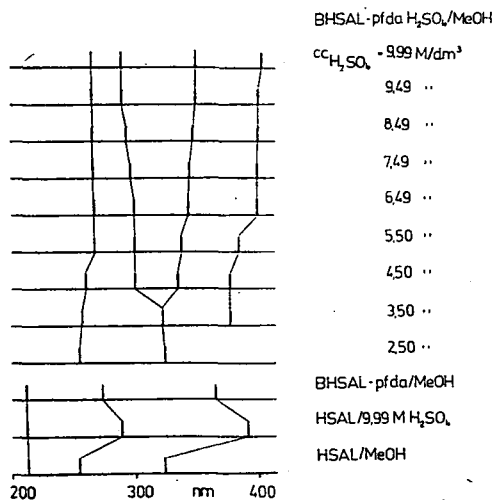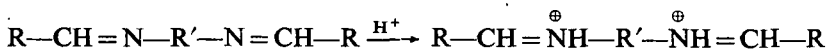

Fig. 6. Schematic representation of spectral changes of BHSAL-pfda in the presence of sulphuric acid of different concentrations in methanol

BHSAL-pfda is only very slightly soluble in the usual solvents and at every acid concentration the spectra show a characteristic change with time (see *e.g.* Fig. 5).
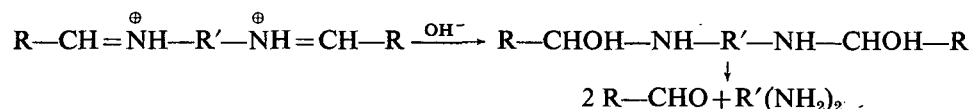
Two ranges are distinguishable between acid concentrations of 4 and ~18 mol/dm³. Between ~18 and ~13 mol/dm³, the spectra show a drastic change

in the range 210—250 nm; a new band develops at 230 nm. Approximate calculations for 18.20, 17.40, 15.60 and 13.70 mol/dm³ acid give half-times of 270, 360, 540 and 720 min, respectively. Below 13.70 mol/dm³ acid this spectral range remains almost unchanged, but above 320 nm a very significant intensity change can be observed. The band-shifts for the calculated $t=0$ spectra are listed in Fig. 6. For the three spectral ranges around 240, 290 and 350 nm, it can be stated that the intensities decrease as the acid concentrations decrease from ~ 18 to ~ 9 mol/dm³; below 9—10 mol/dm³ there is a slight increase in intensity. Below ~ 7 mol/dm³ acid, the spectra correspond to the theoretical curves calculated from the methanolic spectra of the Schiff base components (Fig. 7).

We assumed that in concentrated sulphuric acid the molecules are initially in the cationic form:
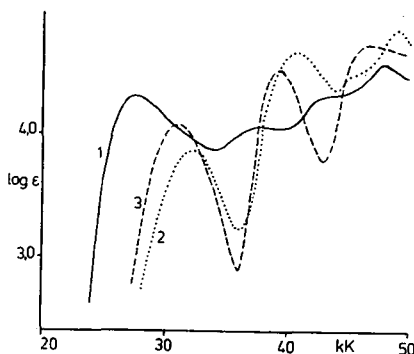

Fig. 7. Comparison of theoretical and experimental absorption curves. 1: BHSAL-pfda in methanol; 2: curve calculated from spectra of methanolic solutions of amine and aldehyde, respectively; 3: absorption curve of the Schiff base in 4.16 mol/dm³ sulphuric acid in methanol

$$R\text{—}CH=N\text{—}R'\text{—}N=CH\text{—}R \xrightarrow{H^+} R\text{—}CH=\overset{\oplus}{N}H\text{—}R'\text{—}\overset{\oplus}{N}H=CH\text{—}R$$

The first step of the transformation would be OH⁻ addition (~ 1 mol/dm³ water is present) and the carbinolamine intermediate would be decomposed, resulting in amine and aldehyde. A strong base should give a conjugated acid with less electropositive character on the nitrogen atom, and consequently this base would be less sensitive to attack by hydroxyl ion. Accordingly, regardless of whether this attack or the decomposition of the carbinolamine intermediate is the rate—determining step, the same inverse relationship may be expected:

$$R\text{—}CH=\overset{\oplus}{N}H\text{—}R'\text{—}\overset{\oplus}{N}H=CH\text{—}R \xrightarrow{OH^-} R\text{—}CHOH\text{—}NH\text{—}R'\text{—}NH\text{—}CHOH\text{—}R$$
$$\downarrow$$
$$2\,R\text{—}CHO+R'(NH_2)_2$$

This mechanism requires further detailed investigations; these are in progress.

Table III

ε_{292} values of solutions with different sulphuric acid contents (mol/dm³)

Compd. \ ^{c}H₂SO₄	17.40	13.95	11.83	9.75	9.06	8.36	6.96	5.57	4.16
BHSAL-ofda	34 200	30 500	26 400	18 600	16 000	12 800	6000	2000	1400
BHSAL-mfda	36 800	28 400	22 500	13 500	10 100	8 000	3300	800	500

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СПЕКТРЫ ШИФФОВЫХ ОСНОВАНИЙ В КОНЦЕНТРИРОВАННОЙ СЕРНОЙ КИСЛОТЕ

Й. Часар

Изучены спектроскопические свойства Шиффовых оснований полученных из салицилальдегида и алкилдиаминов, а также ароматических диаминов в концентрированных растворах серной кислоты (~10−2 mol/dm³). Для распада производных алкилдиаминов получены константы скорости первого порядка. Для o-, m-, и p-фенилендиамино производных найдены два различных явления.