KINETICS AND MECHANISM OF SOLVOLYSIS OF N-ARYL SULFURIC DIAMIDES

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Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

The methanolysis and hydrolysis kinetics have been studied with the following sulfuric diamide derivatives: N-methyl-N-phenyl- (*IIIa*), N-methyl-N-(4-methoxycarbonylphenyl)- (*IIIb*), N-(4-
-methoxycarbonylphenyl)- (*IIIc*), N-methyl-N-(2-methoxycarbonylphenyl)- (*IIId*), N-(2-methoxy-
carbonylphenyl)- (*IIIe*), and N-methyl-N-(2,4-dibromophenyl)- (*IIIf*). The ·solvolyses of the neutral substrates *IIIa* and *IIIb* proceed by the addition-elimination mechanism. In the presence of the solvent lyate ions the solvolyses go by the E1cb mechanism. The solvolyses of the conjugated bases of compounds *IIIa* and *IIIb* are subject to general acid catalysis, the effects of the ring substituents being opposite to those in the addition elimination mechanism. The solvolyses of compounds *IIId* and *IIIf* exhibit a distinct catalytic effect of neighbouring group; the reaction goes via a reactive intermediate, the transformation of the intermediate into the solvolysis product being subject to general acid and base catalysis.

N-Alkyl-1*H*-2,1,3-benzothiadiazin-4-one-2,2-dioxides (*I*) act as selective herbicides, e.g. the 3-isopropyl derivative *Ia* is produced under the commercial name[1,2] Basagran and Bentazon. The last step in the synthesis of these compounds usually consists in cyclization of substituted 2-methoxycarbonylphenylsulfuric diamides (*II*). We
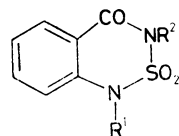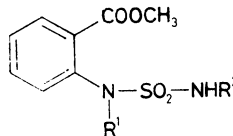

Ia, R¹= H ; R²= CH(CH₃)₂   *II*

have found that during preparation of compounds *II* in protic solvents these compounds are solvolyzed to give methyl N-alkylanthranilates or methyl anthranilate

and solvolysis products of sulfonyl imine $RN=SO_2$. Only two[3,4] of the reports published deal with kinetics and mechanism of the solvolysis of N-arylsulfuric diamides. In one of them[3] the solvolysis is represented as an elimination reaction in which solvent molecules (ROH) act as both acid and base (Scheme 1). In the other paper[4], on the other hand, the solvolysis proceeds as a spontaneous bimolecular
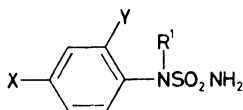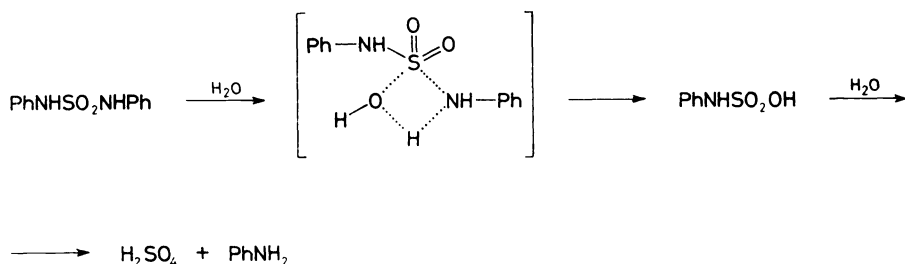

$III\ a,\ R^1 = CH_3;\ X = Y = H$

$III\ b,\ R^1 = CH_3;\ X = COOCH_3;\ Y = H$

$III\ c,\ R^1 = H;\ X = COOCH_3;\ Y = H$

$III\ d,\ R^1 = CH_3;\ X = H;\ Y = COOCH_3$

$III\ e,\ R^1 = H;\ X = H;\ Y = COOCH_3$

$III\ f,\ R^1 = CH_3;\ X = Y = Br$

reaction (Scheme 2). We have found that the solvolyses of compounds *III* proceed by at least three mechanisms depending on the structure of *III*. The results of our kinetic studies are dealt with in the present communication.
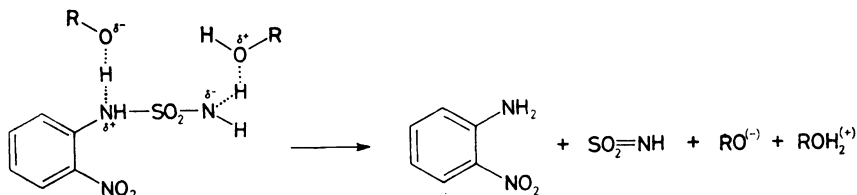
SCHEME 1

SCHEME 2

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra of the compounds were measured at 400·13 and 100·62 MHz (compounds *IIIb—IIIe*) using an AM-400 Bruker spectrometer or at 99·602 and 25·047 MHz (compounds *III a,f*) using a JNM FX-100 (JEOL) apparatus, respectively. The substances to be measured were dissolved in hexadeuteriodimethyl sulfoxide (c. 5% solutions). The chemical shifts are referred to the middle signal of the solvent multiplet — $\delta(^1H)$ 2·55 and $\delta(^{13}C)$ 39·6. For interpretations of the NMR spectra of compounds *IIId,e* we used the sequences APT[5], COSY, and HETCOR[6].

Chlorosulfonyl isocyanate. Sulfur trioxide (1 920 g, 24 mol) was distilled at a rate of 2—3 drops per second into a flask containing 910 ml (1 106 g, 18 mol) liquid cyanogen chloride. The flask was cooled to — 5 to — 15°C. Then the cooling bath was replaced by an oil bath which was gradually heated to 120°C with continuous stirring of the reaction mixture. The cyanogen chloride obtained from the distillation was bubbled back through the reaction mixture. The raw product was distilled off with continuous introducing gaseous cyanogen chloride. Yield of the crude product (b.p. 100—105°C) was 3 000 g (97%). This product was purified by repeated distillation, b.p. 103—105°C, ref.[7] gives b.p. 108°C.

Sulfamoyl chloride (NH_2SO_2Cl). A solution of 14·2 g (0·1 mol) chlorosulfonyl isocyanate in 50 ml dry ether was treated with 1·8 ml (0·1 mol) water acidified with HCl and added dropwise with stirring at — 40°C. Then the temperature was gradually increased up to the room temperature, whereafter the mixture was stirred 1·5 h. The ether was distilled off in vacuum at room temperature, and the evaporation residue was recrystallized from dichloromethane. Yield 9·2 g (80%), m.p. 40—41°C (ref.[7] gives m.p. 40—41°C).

N-Methyl-2,4-dibromoaniline. A solution of 21·4 g (0·2 mol) N-methylaniline in 100 ml acetic acid was treated with 20·5 ml (64 g, 0·4 mol) bromine added dropwise within 30 min with stirring at room temperature. After another 30 min of stirring at 30°C the solution was decolourized by addition of sodium carbonate and diluted with 1 500 ml water. The separated product was recrystallized from methanol. Yield 42 g (79%), m.p. 47—48°C (ref.[8] gives m.p. 48°C).

Methyl 2-methylaminobenzoate. A mixture of 9 g (60 mmol) 2-methylaminobenzoic acid and 120 ml 2·5M methanolic hydrogen chloride was refluxed 7 h. During this time, 8 g thionyl chloride was added drop by drop to the reaction mixture. Thereafter methanol was distilled off, the residue was dissolved in 50 ml water, and pH 8—9 was adjusted by addition of 20% sodium carbonate. The emulsion formed was extracted with 3 × 50 ml ether. The extract was dried with sodium sulfate, ether was distilled off, and the raw product was purified by column chromatography (Al_2O_3, toluene). Yield 4·4 g (44%), the product is pure according to ^{1}H NMR spectrum. ^{1}H NMR: 7·83 dd 1 H (H-6, $J(5, 6) = 8·0$ Hz, $J(4, 6) = 1·6$ Hz); 7·44 m, 1 H (H-4); 6·74 d, 1 H (H-3, $J(3, 4) = 8·5$ Hz); 6·62 m, 1 H (H-5, $J(4, 5) = 8·1$ Hz); 7·60 bq, 1 H (NH); 3·83 s, 3 H (OCH$_3$); 2·88 d, 3 H (NHCH$_3$, $J = 4·2$ Hz). ^{13}C NMR: 168·15 (CO), 151·50 (C-2), 134·82 (C-4), 131·11 (C-6), 114·20 (C-5), 111·01 (C-3), 109·23 (C-1), 51·44 (CH$_3$O), 29·29 (CH$_3$N).

Methyl 4-methylaminobenzoate. A mixture of 10 g (66 mmol) methyl 4-aminobenzoate, 35 ml 1M sodium carbonate, and 8·5 g (67 mmol) dimethyl sulfate was refluxed 30 min, cooled, and the precipitated solid was collected by suction and washed with water. The product was dissolved in 100 ml 18% HCl and the solution was cooled to — 5°C. A solution of 7·5 g (110 mmol) NaNO$_2$ in 20 ml water was added dropwise with stirring. After 5 min the precipitated solid was collected by suction and washed with dilute hydrochloric acid. The wet methyl N-methyl-N-nitroso-4--aminobenzoate (c. 22 g, m.p. 112—115°C) was transferred into methanolic hydrogen chloride (500 ml, c. 2·5 mol l^{-1}) and after addition of 50 ml thionyl chloride the mixture was refluxed

1·5 h. Methanol was distilled off, and the almost dry residue was diluted with water and neutralized to pH 6—7 with sodium carbonate solution. The mixture was cooled in an ice bath and gave 5·3 g product, m.p. 85—92°C. Its column chromatography (Al_2O_3, toluene) gave 3·7 g (34%) product with m.p. 89—92°C (ref.[9] gives m.p. 95·5°C). ^{1}H NMR: 7·70 and 6·56 AA′XX′ multiplet, 2×2 H (Ar); 6·3 b, 1 H (NH); 3·85 s, 3 H (OCH_3); 2·84 d, 3 H ($NHCH_3$, $^3J = 5·0$ Hz).

N-Methyl-N-phenylsulfuric diamide (IIIa). A solution of 6·4 g (60 mmol) N-methylaniline in 25 ml benzene was mixed with a solution of 3·5 g (30 mmol) sulfamoyl chloride in 50 ml benzene at 10°C. After 1 h, the reaction mixture was mixed with 10 ml 6M-NaOH. The separated aqueous layer was acidified with 2M-HCl to pH 2, and the separated crystals were collected by suction and dried in a desiccator. Yield 1·9 g (34%), m.p. 85—88°C. For $C_7H_{10}N_2O_2S$ (186·3) calculated: 45·12% C, 5·41% H, 15·10% N, 17·20% S; found: 45·12% C, 5·26% H, 14·86% N, 17·46% S. ^{1}H NMR: 7·5—7·1 m, 5 H (C_6H_5); 7·1 b, 2 H (NH_2); 3·17 s, 3 H (CH_3). ^{13}C NMR: 143·38 (C-1), 128·82 (C-3, 5), 126·18 (C-2, 4), 38·20 (CH_3).

N-Methyl-N-(4-methoxycarbonylphenyl)sulfuric diamide (IIIb) was prepared by mixing a solution of 1·65 g (10 mmol) methyl 4-methylaminobenzoate in 5 ml benzene with a solution of 0·58 g (5 mmol) sulfamoyl chloride in 10 ml benzene. After 30 min stirring at 20°C, the reaction mixture was cooled to −20°C and then slowly temperated to +10°C. The crystals were immediately collected by suction on a sintered glass filter and washed with petroleum ether, dried by passing air through and washed with 20 ml 0·1M-HCl and then with water until neutral. The product was dried in a desiccator at room temperature to give 0·6 g (49%) compound melting at 135—140°C. For $C_9H_{12}N_2O_4S$ (244·4) calculated: 44·23% C, 4·95% H, 11·51% N, 13·12% S, found: 44·55% C, 5·20% H, 11·80% N, 13·48% S. ^{1}H NMR: 7·99 and 7·53 AA′XX′ multiplet, 2×2 H (Ar); 6·3 b, 2 H (NH_2); 3·89 s, 3 H (OCH_3); 3·24 s, 3 H (NCH_3). ^{13}C NMR: 165·88 (C-O), 147·44 (C-1), 129·71 (C-3), 126·05 (C-4), 124·24 (C-2), 52·10 (OCH_3), 37·37 (NCH_3)
The other substances were prepared similarly as *IIIb*.

N-(4-Methoxycarbonylphenyl)sulfuric diamide (IIIc). Yield 57%, m.p. 175—177°C. For C_8H_{10}·N_2O_4S (230·3) calculated: 41·71% C, 4·38% H, 12·21% N, 13·92% S; found: 42·01% C, 4·51% H, 11·89% N, 13·66% S. ^{1}H NMR: 7·91 and 7·26 AA′XX′ multiplet, 2×2 H (Ar); 7·6 b, 3 H (NH, NH_2); 3·85 s, 3 H (OCH_3). ^{13}C NMR: 166·06 (CO), 144·45 (C-1), 130·38 (C-3), 122·14 (C-4), 116·52 (C-2), 51·80 (OCH_3).

N-Methyl-N-(2-methoxycarbonylphenyl)sulfuric diamide (IIId). Yield 19%, m.p. 105—110°C. For $C_9H_{12}N_2O_4S$ (244·4) calculated: 44·23% C, 4·95% H, 11·51% N, 13·12% S; found: 44·52% C, 5·19% H, 11·78% N, 13·21% S. ^{1}H NMR: 7·71 d, 1 H (H-3, $J(3, 4) = 7·7$ Hz); 7·65 t, 1 H (H-5, $J(4, 5) = 7·6$ Hz); 7·58 d, 1 H (H-6); 7·45 t, 1 H (H-4, $J(4, 6) = 1·4$ Hz); 7·0 b, 2 H (NH_2) 3·84 s, 3 H (OCH_3); 3·17 s, 3 H (NCH_3). ^{13}C NMR: 166·62 (CO), 141·70 (C-1), 131·75 (C-2), 132·22, 129·79, 127·92, 127·28 (Ar), 52·07 (OCH_3), 38·69 (NCH_3).

N-(2-Methoxycarbonylphenyl)sulfuric diamide (IIIe). A solution of 4·3 g (20 mmol) N-(2-carboxyphenyl)sulfuric diamide in 150 ml ether was stirred, and a solution of diazomethane in ether was added thereto drop by drop until a constant yellow colour of the mixture. The excess diazomethane was removed by shaking with 20 ml dilute hydrochloric acid (1 : 1). The ether layer was washed with water, dried, and distilled in vacuum until dry. Yield 2·5 g (54%), m.p. 128 to 130°C (methanol). For $C_8H_{10}N_2O_4S$ (230·3) calculated: 41·71% C, 4·38% H, 12·21% N; 13·92% S; found: 42·00% C, 4·50% H, 12·03% N, 14·12% S. ^{1}H NMR: 8·4 b, 3 H (NH, NH_2) 8·02 d, 1 H (H-3, $J(3, 4) = 7·7$ Hz); 7·68 m, 1 H (H-5); 7·67 m, 1 H (H-6); 7·16 m, 1 H (H-4); 1 H (H-4); 3·95 s, 3 H (OCH_3). ^{13}C NMR: 168·17 (CO), 141·55 (C-1), 134·84 (C-5), 130·98 (C-3), 121·53 (C-6), 117·44 (C-4), 113·90 (C-2), 52·71 (OCH_3).

N-Methyl-N-(2,4-dibromophenyl)sulfuric diamide (IIIf). A mixture prepared by mixing a solution of 5·8 g (22 mmol) N-methyl-2,4-dibromoaniline in 10 ml benzene and 1·25 g (11 mmol) sulfamoyl chloride in 20 ml benzene was stirred at room temperature 1 h. The product was extracted with 4 ml 6M-NaOH, and the extract was acidified to pH 2 by addition of 2M-HCl. The separated solid was collected by suction and dried to give 2·2 g (58%) product with m.p. 141—143°C. For $C_7H_8Br_2N_2O_2S$ (344·1) calculated: 24·43% C, 2·34% H, 8·18% N, 9·32% S, found: 24·41% C, 2·41% H, 7·94% S. ^1H NMR: 7·98 d, 1 H (H-3, $J(3, 5) = 2·0$ Hz); 7·69 dd 1 H (H-5, $J(5, 6) = 8·6$ Hz); 7·59 d, 1 H (H-6); 7·22 b, 2 H (NH$_2$); 3·07 s, 3 H (NCH$_3$). ^{13}C NMR 141·69 (C-1), 135·13 and 131·62 (C-3, C-5), 130·57 (C-6), 125·54 and 121·03 (C-2, C-4), 38·31 (NCH$_3$).

Kinetic Measurements

The rates of the solvolyses were measured spectrophotometrically using a Specord UV-VIS (Zeiss, Jena) apparatus and adopting methanolic or aqueous buffer solutions, methanolic methoxide or hydrochloric acid solutions. The ionic strength of methanolic media was adjusted at $I = 0·125$ mol l^{-1} by addition of 0·125 mol l^{-1} methanolic NaCl solution, that of the aqueous buffers was adjusted at $I = 1$ mol l^{-1} by addition of 2M-KCl.

At the temperatures of 25 to 40°C, the kinetic runs were carried out in such way, that 2 ml buffer, HCl or methoxide was placed into a quartz cell and tempered, and 25 μl methanolic solution of the substrate (c. 5 . 10^{-3} mol l^{-1}) was injected thereinto at the time $t = 0$, whereupon the absorbance was measured at definite time intervals at suitable wavelengths (Table I). In the case of experiments carried out at or above 60°C, 25 μl c. 5 . 10^{-2} mol l^{-1} methanolic substrate solution was added to 25 ml buffer or HCl solution. Aliquots of this mixture were transferred into glass ampoules and placed in a thermostat. At definite time intervals individual ampoules were cooled, opened, the solution was transferred into a cell and its absorbance was measured at a suitable wavelength. The rate coefficients k_{obs} (s^{-1}) were calculated from the equation $k_{obs}t = -2·3 \log \Delta A + const$, $\Delta A = (A_\infty - A_t)$ or $(A_t - A_\infty)$.

TABLE I

The equilibrium constants K and pK_a and the solvolysis rate coefficients k_0 (s^{-1}) and k_A (l mol^{-1} . . s^{-1}) of compounds *IIIa—IIIc* and *IIIf* measured in water and methanol at 25°C at the given wavelength λ (nm)

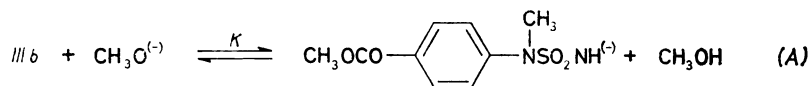| Compound	Medium	$k_0 . 10^6$	$k_A . 10^4$	λ	K	pK_a	λ
IIIa	H$_2$O	0·072 ± 0·003	3·56 ± 0·20	285	—	10·34 ± 0·07	245
	CH$_3$OH	0·76 ± 0·04	6·50 ± 0·40	250	45	15·27 ± 0·05	250
IIIb	H$_2$O	5·60 ± 0·30	1·50 ± 0·06	305	—	9·87 ± 0·06	294
	CH$_3$OH	52·00 ± 3·00	2·00 ± 0·10	262	100	14·92 ± 0·06	303
IIIc	H$_2$O	—	—	—	—	8·38 ± 0·04	305
	CH$_3$OH	0·23 ± 0·10	—	295	2 350	13·55 ± 0·05	305
IIIf	H$_2$O	—	—	—	—	10·26 ± 0·04	255
	CH$_3$OH	7·00 ± 0·50	0·132 ± 0·007	312	150	14·74 ± 0·07	270

Measurement of Dissociation Constants

The dissociation constants of compounds *IIIa—IIIf* were measured with the Specord UV-VIS spectrophotometer at 25°C. The measurements were carried out in aqueous carbonate and borate buffers ($I = 1$ mol 1^{-1}) and in methanolic solutions of sodium methoxide ($I = 0.125$ mol. $.1^{-1}$). Usually, 1·6 ml buffer solution (the ionic strength was adjusted by addition of KCl or NaCl) or methoxide solution was placed into a 1 cm quartz cell and after attaining the required temperature, 0·4 ml substrate solution of the same temperature was added. The spectra measured for each buffer series (230—370 nm) exhibited isosbestic points. If in the buffer given the substrate underwent solvolysis with a half-life below c. 40 min, extrapolation to the zero time was carried out for the given analytical wavelength (Table I). The pH values of aqueous buffers were determined with the use of a MV 870 apparatus (VEB Präcitronic, G.D.R.) and a glass and a silver chloride electrodes.

RESULTS AND DISCUSSION

Solvolyses of Compounds IIIa—IIIc

The methanolysis rate of N-methyl-N-(4-methoxycarbonylphenyl) sulfuric diamide (*IIIb*) was measured at 262 nm in a series of acetate buffers (the component ratios 4 : 1 to 1 : 4; six concentrations of the buffer), in methanolic HCl ($5 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ mol 1^{-1}), and in methoxide solutions at 25°C. The value of the observed rate coefficient $k_0 = (5 \cdot 2 \pm 0 \cdot 3) \cdot 10^{-5}$ s^{-1} was independent of the buffer concentration and the buffer component ratio or of concentration of hydrogen chloride. In the methoxide solutions compound *IIIb* is dissociated with a constant $K = 100$

$$III\,b \;+\; CH_3O^{(-)} \;\overset{K}{\rightleftharpoons}\; CH_3OCO\!-\!\!\left\langle\!\!\bigcirc\!\!\right\rangle\!\!-\!\!\underset{\displaystyle NSO_2\,NH^{(-)}}{\overset{\displaystyle CH_3}{|}} \;+\; CH_3OH \qquad (A)$$

(Eq. (A)). At increasing methoxide concentration the methanolysis rate increases non-linearly (Fig. 1). The theoretical curve in Fig. 1 was calculated from Eq. (1),

$$k_{obs} = (1 + K[CH_3O^{(-)}])^{-1} (k_0 + k_A K[CH_3O^{(-)}]), \qquad (1)$$

where k_A means the rate constant of methanolysis of the anion of ester *IIIb* ($k_A = = 2 \cdot 0 \pm 0 \cdot 1$ l mol^{-1} s^{-1}).

The methanolysis of N-methyl-N-phenylsulfuric diamide (*IIIa*) was followed at 250 nm at the temperatures of 25 and 70°C in a series of acetate buffers with the component ratio 1 : 1 and in methoxide solutions. The rate coefficients k_0 at 25 and 70°C have the values of $(7 \cdot 6 \pm 0 \cdot 4) \cdot 10^{-7}$ s^{-1} and $(2 \cdot 06 \pm 0 \cdot 03) \cdot 10^{-4}$ s^{-1}, respectively. In methoxide solutions the dependence of the reaction rate on methoxide concentration had a similar shape as that of compound *IIIb* (Fig. 1).

The methanolysis of N-(4-methoxycarbonylphenyl)sulfuric diamide (*IIIc*) was studied in a series of acetate buffers (1 : 1) at four temperatures: at 70, 81·5, 91·5, and 99°C the k_0 rate constants have the values of $1·34 . 10^{-4}$, $5·78 . 10^{-4}$, $13·6 . 10^{-4}$, and $24·0 . 10^{-4} s^{-1}$, respectively. Extrapolation to 25°C gave the value $k_0 = = (2·3 \pm 1·0) . 10^{-7} s^{-1}$. In methoxide solutions at 25°C it was only possible to measure the equilibrium constant K, because the solvolysis is very slow. The values of all the rate and equilibrium constants are presented in Table I.

The methanolysis kinetics of compound *IIIa* was also studied in butylamine buffers ($[C_4H_9NH_2]/[C_4H_9NH_3Cl]$ = 2 or 1; five buffer concentrations always). In these buffers the concentration of ester *IIIa* is by several orders higher than that of its anion. The observed rate coefficient of methanolysis k_{obs} depends on the butyl-ammonium concentration as follows:

$$k_{obs} = a + b[C_4H_9\overset{(+)}{NH_3}] . \tag{2}$$

The intercept a is defined by Eq. (3) and the slope b by Eq. (4),

$$a = k_0 + k_A K[CH_3O^{(-)}] \tag{3}$$

$$b = k_{BH} K[CH_3O^{(-)}] , \tag{4}$$

where k_{BH} means the methanolysis rate constant of the anion of compound *IIIa* catalyzed by butylammonium ion. For two butylamine buffers used (2 : 1 and 1 : 1) we determined the values $a = 1·8 . 10^{-6} s^{-1}$ and $1·1 . 10^{-6} s^{-1}$, respectively, and $b = 3·6 . 10^{-5} 1 mol^{-1} s^{-1}$ and $1·75 . 10^{-5} 1 mol^{-1} s^{-1}$, respectively. Table I also presents the rate coefficients k_0 of the hydrolyses of compounds *IIIa* and *IIIb* mea-
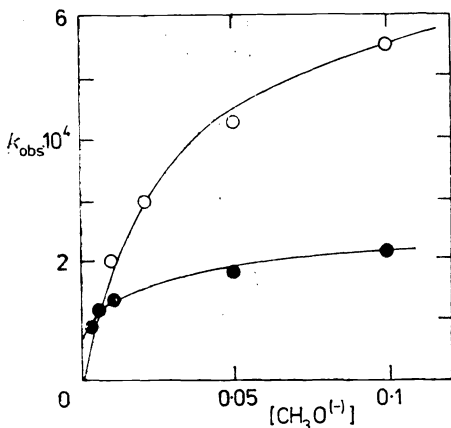

FIG. 1

The dependence of the methanolysis rate coefficient $k_{obs}(s^{-1})$ of compounds *IIIa* (○) and *IIIb* (●) on the methoxide concentration $[CH_3O^{(-)}]$ $(mol\ l^{-1})$ at 25°C

sured in phosphate buffers (pH 6·7; 25°C) at 285 and 305 nm, respectively, and the values of dissociation constants of these substances measured in carbonate buffers, and the dissociation constant of compound *IIIc* measured in borate buffers. The rate constant k_A (Table I) of hydrolysis of anion of *IIIa* was measured in hydroxide solutions. At these conditions, predominantly the ester group of compound *IIIb* underwent the hydrolysis.

In carbonate buffers (compound *IIIb*) and butylamine buffers (compound *IIIa*) (Fig. 2) the hydrolysis of the substrates themselves is much slower than that of their anions. The observed hydrolysis rate coefficient k_{obs} obeys Eq. (5).

$$k_{obs} = K(k_A + k_{BH}[BH]/(K + a_H)) \tag{5}$$

The rate constant value of hydrolysis of anion of *IIIb* (k_A, Table I) was estimated by extrapolation to the zero buffer concentration. The catalytic rate constants k_{BH} have the values of $(3·8 \pm 0·2) . 10^{-4} \, \mathrm{l \, mol^{-1} \, s^{-1}}$ for butylammonium ion and compound *IIIa*, and of $(7·5 \pm 0·8) . 10^{-4} \, \mathrm{l \, mol^{-1} \, s^{-1}}$ for hydrogencarbonate ion and compound *IIIb*.

The solvolyses of neutral compounds *IIIa* and *IIIb* are catalyzed neither by acidic nor by basic buffer components. The value of methanolysis rate constant k_0 of ester *IIIb* is almost 2 orders higher than that for ester *IIIa*. Hence, the methanolysis cannot go by the mechanism given in Scheme 1. Even if the N—H bond were almost completely split and the proton-transfer were advanced to a negligible extent in the transition state of the reaction going according to Scheme 1, the maximum ratio of the rate coefficients k_0 would be determined by the ratio of equilibrium constants of the two compounds $(K(IIIb)/K(IIIa) = 2·2$ in methanol). In water, the ratio of the rate coefficients would be about 3. The solvolyses of compounds *III* must
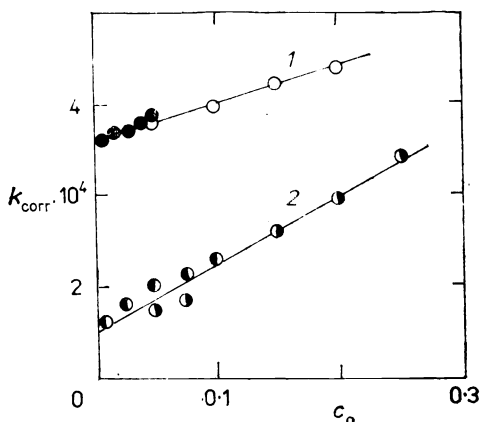

FIG. 2

The dependence of the hydrolysis rate coefficients $k_{corr}(s^{-1})$ ($k_{corr} = k_{obs}(1 + (a_H/K_A))$ of compounds *IIIa* (line *1*) and *IIIb* (line *2*) on the concentration of acidic component of buffer c_{HB}(mol l^{-1}) for acidic 1 : 4 carbonate buffer (◑), 1 : 1 carbonate buffer (◐), acidic 1 : 4 butylamine buffer (○), and 1 : 1 butylamine buffer (●)

involve the addition of solvent to the sulfur atom. According to Scheme 2, this addition is coupled with the N—S bond splitting and with the proton-transfer from a water molecule to the nitrogen atom. We suppose that the stepwise addition-elimination


PhNHCH$_3$ +   ROSO$_2$NH$_2$
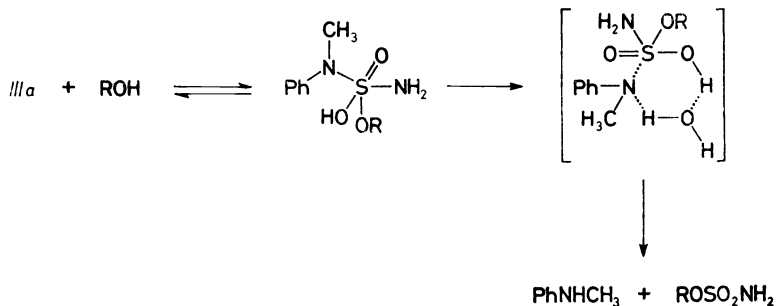
SCHEME 3

mechanism given in Scheme 3 is more likely for the following reasons: (i) The ϱ constant value estimated from the solvolysis rate coefficients (k_0) of compounds $IIIa$ and $IIIb$ (for CO$_2$CH$_3$ it is $\sigma_p^- = 0.74$; ref.[10]) is $\varrho \sim 2.6$. This value is close to that for the dissociation of anilinium ions[11], which means that the effective negative charge in the activated complex[12] is almost by one unit higher than that in the starting sulfuric diamide (rather in accordance with Scheme 3). (ii) The nucleophilic substitution at the sulfur atom of X—SO$_2$—NH$_2$ group goes by the stepwise addition elimination mechanism[13-15]. The concerted pathway is conceivable only with very good leaving groups[16].

The presence of acidic proton in –SO$_2$H group has the consequence that the S—N bond splitting does not need any external acidic catalyst.

In solutions containing lyate ions the ratio of the solvolysis rate constants of compounds $IIIa$ and $IIIb$ is reversed. The ratio of the rate constants k_A of the solvolyses of the anions of compounds $IIIa$ and $IIIb$ is 0.42 in water and 0.31 in methanol. Two mechanisms are conceivable for the methanolysis of the anions (Schemes 4 and 5). The first phase of the mechanism given in Scheme 4 is similar to the solvolysis mechanism in neutral medium (Scheme 3) with the difference that RO$^{(-)}$ is added instead of ROH. The intermediate is negatively charged and it should be stabilized more than the neutral intermediate by methoxycarbonyl group. In the second step the intermediate is decomposed into products. The splitting off of the amine is subject to general acid catalysis. In the absence of buffers, only the solvent molecules (ROH) can act as the catalyst acid, they are of course much weaker than the –SO$_3$H groups in the neutral intermediate (Scheme 3). In the methanolysis going via the neutral intermediate, even the proton of the lyonium ion of solvent (CH$_3$OH$_2$)$^{(+)}$
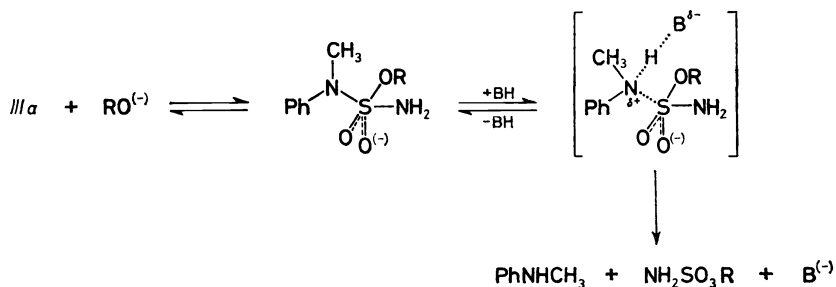
SCHEME 4

$$(+)$$
cannot effectively compete with the proton of the $-SO_2H$ group, although CH_3OH_2 is almost a 20 orders stronger acid than CH_3OH. This means that the protonation of the leaving amino group by methanol in the case of the negatively charged intermediate (Scheme 5) operates far less than in the case of the neutral intermediate (Scheme 3).


$$SO_2=NH \ + \ ROH \ \longrightarrow \ NH_2SO_3R \qquad\qquad R = H \ ; \ CH_3$$
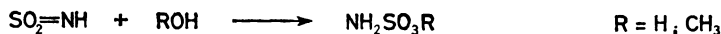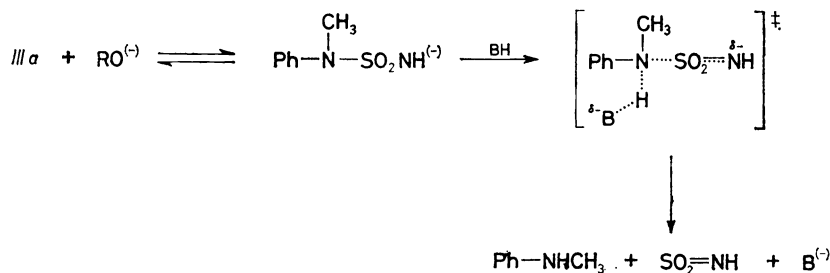
SCHEME 5

Both the factors given (the addition of $RO^{(-)}$ and the protonation of intermediate by methanol) should have the consequence that the activated complex of the solvolysis going via the negatively charged intermediate would carry a greater negative charge at nitrogen than that in the activated complex of the solvolysis of the neutral substance. Due to that, the ratio of the rate constants k_A of compounds *IIIa* and *IIIb* should be still greater than that of the k_0 constants. In reality, however, the ratio $k_A(IIIb)/k_A(IIIa)$ is less than 1, which means that the solvolysis must go by the E1cb mechanism such as that given in Scheme 5. As compared with hydrogen, the methoxy-carbonyl group slows down the decomposition of the intermediate into the solvolysis

products. The substituent at para position of the benzene ring (H or COOCH$_3$) "sees" in the activated complex, a somewhat smaller negative charge (or a somewhat larger positive charge) at the nitrogen of phenylamino group than it does in the substrate anion. Therefrom it follows that in the activated complex (Scheme 5) the proton transfer to the nitrogen of phenylamino group is equally or even more advanced as compared with the N—S bond splitting.

The mechanism of lyate-ion-catalyzed solvolysis of compounds *IIIa* and *IIIb* can be compared with the mechanisms of hydrolysis of 4-nitrophenyl sulfamate *IV* (ref.[17]) and of anion of N-methyl-N-phenylsulfamic acid *V* (ref.[18]). The hydrolysis of compound *IV* goes by the E1cb mechanism. 4-Nitrophenoxy group is a very good

OSO$_2$NH$_2$ CH$_3$—N—SO$_3^{(-)}$

NO$_2$

IV   *V*
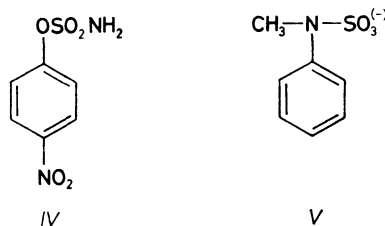
leaving group (nucleofuge), hence it does not require any assistance by acid in the transition state. The hydrolysis of anion *V* is general-acid-catalyzed. The –SO$_3^-$ group is a much worse electrofuge than –SO$_2$NH$^-$. Therefore, nitrogen atom of compound *V* is protonated in a pre-equilibrium, whereupon the –SO$_3^-$ group is split off with the assistance by a water molecule in the rate-limiting step. The solvolysis mechanism of the anions of compounds *IIIb* and *IIIc* lies between these extremes.

Methanolyses of Compounds IIId – IIIf

The methanolysis of N-methyl-N-(2-methoxycarbonylphenyl)sulfuric diamide (*IIId*) was studied at 25°C in acetate, chloroacetate, and dichloroacetate buffers (Table II, Figs 3 and 4) and in methanolic hydrochloric acid (2·5 . 10^{-3} to 5 . 10^{-2} mol l^{-1}).

In the methanolic HCl the methanolysis rate coefficient is independent of the acid concentration and its value is $k_{obs} = (1·90 \pm 0·15) . 10^{-3}$ s^{-1}. The methanolysis rate exhibits a nonlinear increase with increasing buffer concentration in all the buffers used. The values of rate coefficients limit to the k_{obs} value measured in the solutions of hydrogen chloride.

The course of methanolysis can be simply expressed by Scheme 6 where P means buffer. The rate coefficient k_{obs} is defined by Eq. (6) where k_p means the rate constant

$$k_{obs} = \frac{k_1 k_p[P]}{k_{-1} + k_p[P]} = \frac{k_1}{(k_{-1}/k_p[P]) + 1} \tag{6}$$
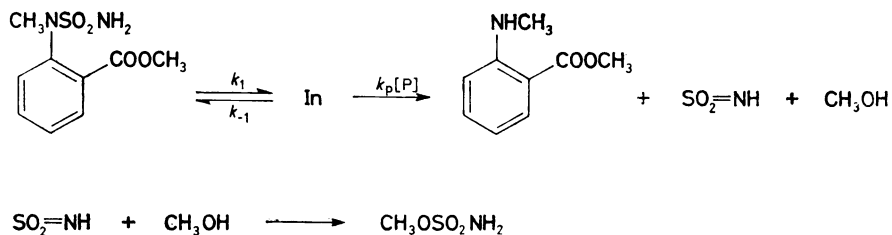
SCHEME 6

of the buffer-catalyzed transformation of the intermediate In, and k_1 and k_{-1} are the rate constants of formation and reverse reaction, respectively, of the intermediate In $(k_1 = 1 \cdot 9 \, . \, 10^{-3} \, \text{s}^{-1})$. The values k_p/k_{-1} given in Table III were used for the calculation of the dependence of k_{obs} on the buffer concentration $[P]$. In the acetate buffers, the k_p/k_{-1} value increases with the buffer basicity. In the chloroacetate buffers, on the other hand, this ratio decreases. This means that in both the buffers, catalysis by both the basic and the acidic components of the buffers is significant. In acetate buffers the base catalysis is more significant, whereas in chloroacetate buffers the acid catalysis predominates.
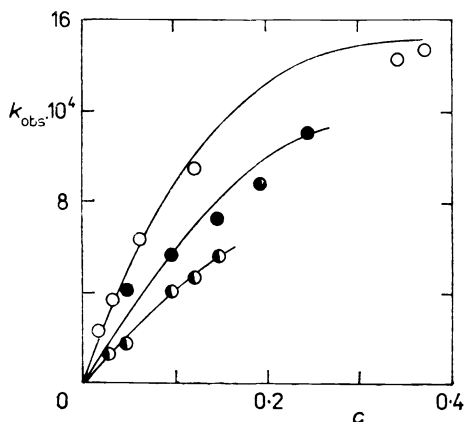

FIG. 3

The dependence of the methanolysis rate coefficients $k_{obs}(\text{s}^{-1})$ of compound *IIId* on the buffer concentrations $c_{buffer}(\text{mol} \, \text{l}^{-1})$ in chloroacetate buffers: acidic 1 : 4 (○), 1 : 1 (●), and basic 1 : 4 (◐)
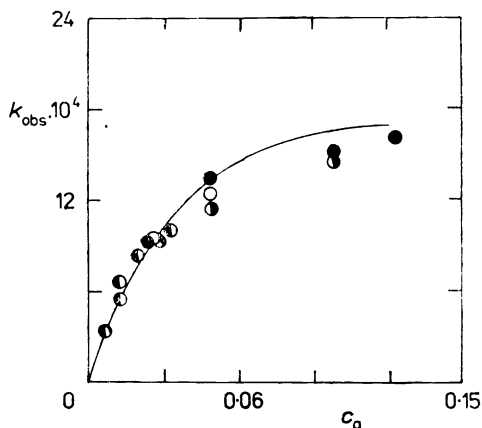
FIG. 4

The dependence of the methanolysis rate coefficients $k_{obs}(\text{s}^{-1})$ of compound *IIId* on the acid concentration in dichloroacetate buffers: basic 1 : 4 (◐), 1 : 1 (●), acidic 1 : 4 (○), and acidic 1 : 2 (◑)

Figure 5 presents the dependence of the k_p/k_{-1} ratio on the proportion of acid in buffer $([HB]/([HB] + [B]))$. The linear dependence is defined by Eq. (7). The values of k_p/k_{-1} ratio extrapolated to the limit values of 0 and 1 for the

TABLE II

The methanolysis rate coefficients k_{obs} (s^{-1}) of compound *IIId* in acetate buffers with concentration c_p (mol l^{-1})

A^a							
1		0·25		0·5		4	
c_p	$k_{obs} \cdot 10^4$	c_p	$k_{obs} \cdot 10^4$	c_p	$k_{obs} \cdot 10^4$	c_p	$k_{obs} \cdot 10^4$
0·05	2·60	0·063	2·15	0·075	3·10	0·063	3·60
0·10	3·90	0·130	3·40	0·150	5·45	0·094	5·25
0·20	7·20	0·350	6·68	0·225	7·20	0·125	6·00
0·25	8·75	0·375	8·90	0·300	7·95	0·155	7·50
—	—	0·500	10·15	0·380	9·50	—	—

^{a} $A = [CH_3COONa]/[CH_3COOH]$.

TABLE III

The ratios of rate coefficients k_p/k_{-1}, k_{HB}/k_{-1}, and k_B/k_{-1} (l mol^{-1}) of methanolysis of compounds *IIId* in acetate (A), chloroacetate (C), and dichloroacetate buffers (D) for various ratios of the buffer components $[HB]/[B^-]$

Buffer	$[HB]/[B^-]$	k_p/k_{-1}	k_{HB}/k_{-1}	k_B/k_{-1}
	4			
	2	1·70		
A	1	2·40	1·1	4·75
	0·25	2·95		
		3·85		
	4			
	1	7·14		
C		4·55	9·0	0·8
	0·25	2·60		
	4	265	330	—
D	0·25	65		

$$\frac{k_p}{k_{-1}} = \frac{k_{HB}}{k_{-1}} \frac{[HB]}{[HB] + [B]} + \frac{k_B}{k_{-1}} \left(1 - \frac{[HB]}{[HB] + [B]}\right) \qquad (7)$$

proportion of acid in buffer express the ratios k_B/k_{-1} and k_{BH}/k_{-1}, respectively (Table III). The rate constants k_B and k_{HB} correspond to the transformations of the intermediate In catalyzed by the basic and acidic buffer components, respectively (Scheme 6). In dichloroacetate buffers only the acid catalysis is operating (Fig. 4).

N-(2-Methoxycarbonylphenyl)sulfuric diamide (*IIIe*) undergoes methanolysis several orders more slowly than the corresponding N-methyl derivative *IIId*. There-fore, the kinetic measurements were carried out at the temperatures of 60, 70, 75, and 80°C in acetate buffers and at 70°C in methanolic HCl $(5 . 10^{-3}$ to $8 . 10^{-2}$ mol . . $1^{-1})$. The methanolysis rate is independent of the concentration of hydrogen chloride $(k_{obs} = (8 \cdot 0 \pm 0 \cdot 4) . 10^{-4} \text{ s}^{-1})$. The following values of rate coefficients were found for various concentrations of the acetate buffer with the components ratio of $1 : 1$ at 70°C: $5 \cdot 25 . 10^{-4} \text{ s}^{-1}$ $(0 \cdot 0125 \text{ mol } 1^{-1})$, $6 \cdot 1 . 10^{-4} \text{ s}^{-1}$ $(0 \cdot 025 \text{ mol } 1^{-1})$, $7 \cdot 0$ . . 10^{-4} s^{-1} $(0 \cdot 10 \text{ mol } 1^{-1})$, and $7 \cdot 7 . 10^{-4} \text{ s}^{-1}$ $(0 \cdot 20 \text{ mol } 1^{-1})$. The dependence of k_{obs} on buffer concentration is of similar type as that for compound *IIId*, but it converges much more rapidly to the value $k_{obs} = k_1 = 8 . 10^{-4} \text{ s}^{-1}$, which means that the k_p/k_{-1} ratio has a much greater value for compound *IIIe* than for its methyl deriva-tive *IIId*.
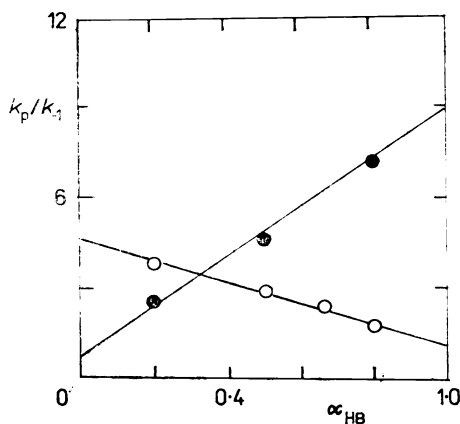

FIG. 5

The dependence of k_p/k_{-1} ratio of methano-lysis of compound *IIId* upon the proportion of acid in buffer $(\alpha_{HB} = [HB]/([HB] + [B^-]))$: acetate buffer $(\bigcirc)$, chloroacetate buffer $(\bullet)$
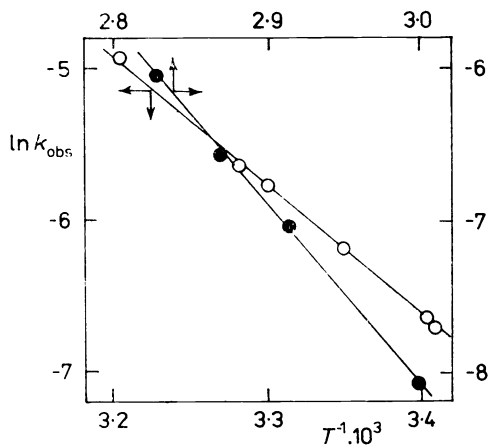
FIG. 6

The dependence of the acid-catalyzed methanolysis rate coefficient $\ln k_{obs}(\text{s}^{-1})$ of compounds *IIId* $(\bigcirc)$ and *IIIe* $(\bullet)$ upon the temperature (K^{-1})

With both the esters, *IIId* and *IIIe*, we examined the dependence of $\ln k_1$ on $1/T$ in methanolic HCl (Fig. 6). The k_1 value found for the compound *IIIe* by extrapolation of the dependence to the temperature of 25°C, $k_1 = (7 \pm 2) \cdot 10^{-6} \text{ s}^{-1}$, is almost 2·5 orders lower than that for the methyl derivative *IIId*.

The rates of base-catalyzed methanolyses of the esters *IIId* and *IIIe* cannot be measured, since the compounds prefer to undergo cyclization (Eq. (B)).

$$III\,d, III\,e \quad \xrightarrow{\text{base}} \quad CH_3OH \;+\; \text{[structure]} \qquad (B)$$

III e , R = H
III d , R = CH$_3$
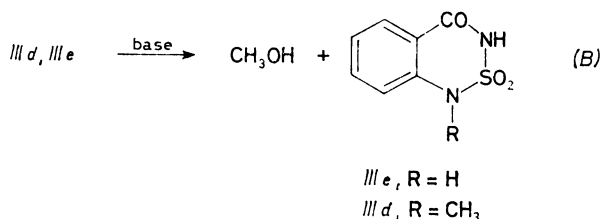
The dependence of the methanolysis rate of the dibromo derivative *IIIf* on methoxide concentration has a similar character as that in the case of ester *IIIb*. The rate constants k_0 and k_A (Table II) are almost one order lower than those for the 4-methoxycarbonyl derivative *IIIb*.

The dependence of methanolysis rate of compound *IIIf* upon the ratio of components and the concentration of acetate buffers (Fig. 7) and upon the hydrogen chloride concentration (Fig. 8) were measured at 70°C. The methanolysis of the dibromo derivative *IIIf* also involves a noncatalyzed (or solvent-catalyzed) reaction, hence k_{obs} is defined by Eq. (8) in acetate

$$k_{obs} = \frac{k_1(k_p[P] + k_0)}{k_{-1} + (k_p[P] + k_0)} = \frac{k_1}{1 + ([P]\,k_p/k_{-1} + (k_0/k_{-1}))^{-1}} \qquad (8)$$

buffers. An analogous equation also holds for the methanolysis of compound *IIIf* in solutions of hydrogen chloride with the difference that k_p and $[P]$ are replaced by k_H and $[H^+]$, resp. Table IV gives the values of the ratios k_p/k_{-1} and k_0/k_{-1} used for the calculation of theoretical dependence of k_{obs} vs $[P]$. In the calculation of the theoretical curve we used also the values $k_1 = 1·1 \cdot 10^{-3} \text{ s}^{-1}$, $k_H/k_{-1} = 33 \text{ l mol}^{-1}$ and $k_0/k_H = 7 \cdot 10^{-4} \text{ mol l}^{-1}$. The dependence of k_p/k_{-1} on the proportion of acid in buffer $([HB]/([HB] + [B]))$ is presented in Fig. 7, wherefrom we estimated the values of ratios $k_{HB}/k_{-1} = 0·2 \text{ l mol}^{-1}$ and $k_B/k_{-1} = 2·9 \text{ l mol}^{-1}$.

In the acetate buffer with $[CH_3COOH] = [CH_3COONa] = 0·1 \text{ mol l}^{-1}$ we measured the methanolysis rate constants of compound *IIIf* at the temperature of 60, 65·5, 70, and 80°C. The calculated values of activation energy and entropy are given in Table V.

The methanolysis mechanism of N-methyl-N-(2-methoxycarbonylphenyl)sulfuric diamide $(IIId)$ is quite different from that of N-methyl-N-fenylsulfuric diamide $(IIIa)$ and of N-methyl-N-(4-methoxycarbonylphenyl)sulfuric diamide $(IIIb)$. Whereas the methanolysis of the neutral compounds $IIIa$ and $IIIb$ is equally fast in buffers and in methanolic hydrogen chloride, that of compound $IIId$ is accelerated by the proton and by acidic and basic components of buffer. The non-catalyzed solvolysis of compound $IIId$ is (due obviously to the steric effect of $-CO_2CH_3$ group) much slower than the same reaction of compound $IIIb$. On the other hand, in methanolic hydrogen chloride the compound $IIId$ is methanolyzed faster than $IIIb$ by a factor of 40 $(k_{obs} = k_1)$.

The formation of reactive intermediate In (Scheme 6) is catalyzed neither by the proton nor by basic and acidic components of buffer. Therefrom it follows that the formation of this intermediate must be enabled by a specific effect of the *ortho*-standing methoxycarbonyl group. A number of cases are given in literature[15,19–21] describing hydrolyses of sulfuric diamides structurally similar to compound $IIId$ where a large rate increase was observed due to the presence of an *ortho*-standing $-CO_2H$ or $-CR_2OH$ group. These hydrolyses involve intramolecular nucleophilic catalysis, cyclic intermediates with hexavalent sulfur (VI) being usually formed[20].
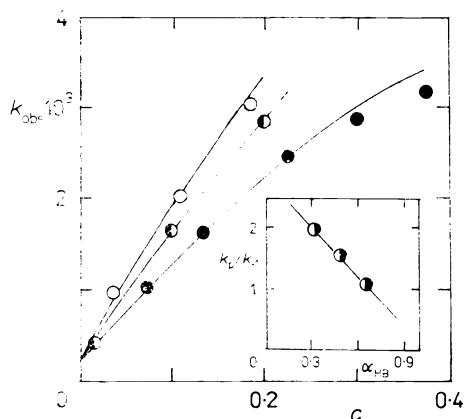

FIG. 7

The dependence of the methanolysis rate coefficients $k_{obs}(s^{-1})$ of the dibromo derivative $IIIf$ upon the concentration of acetate buffers (mol l^{-1}): acidic 1 : 2 (●), basic 1 : 2 (○), 1 : 1 (◑) and the dependence of the k_p/k_{-1} ratio upon the proportion of acid in buffer α_{HB} at 70°C (◐)
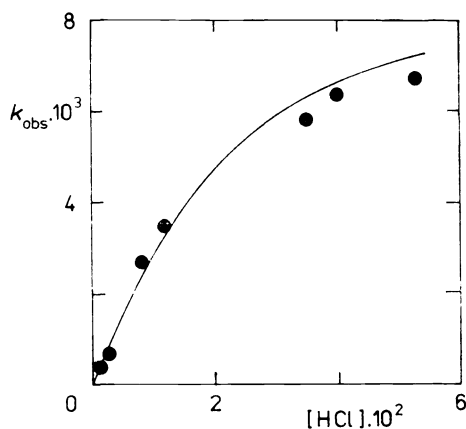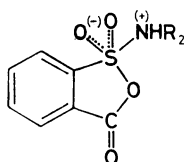
FIG. 8

The dependence of the methanolysis rate coefficient $k_{obs}(s^{-1})$ of the dibromo derivative $IIIf$ upon the concentration of hydrogen chloride (mol l^{-1}) at 70°C

VI

The effective molarity[22] of carboxyl group is as high as 10^{10} mol l^{-1} in favourable cases[15,20]. Considerable anchimeric effects of ester group was found e.g. in the case of substituted benzhydryl bromides: the *o*-ethoxycarbonyl derivative is hydrolyzed much faster than the corresponding *p*-derivative[23].

The transformation of the intermediate In (Scheme 6) into products is catalyzed by both acids and bases. Hence, the intermediate possesses both a considerably acidic hydrogen and a basic centre. On the basis of these findings it is possible to suggest the solvolysis mechanism of compound *IIId* as in Scheme 7. The structure *VII* represents the activated complex (or an unstable intermediate). The proton of NH_2 group in the intermediate In is much more acidic than that in the starting substrate *IIId*, since the oxygen of the newly-formed S—O bond is a much stronger electron acceptor than is the nitrogen in the S—N bond broken. On the other hand, the

TABLE IV

The ratios of methanolysis rate coefficients k_p/k_{-1} (l mol^{-1}) and k_0/k_{-1} of compound *IIIf* in acetate buffers for various ratios of the buffer components $B = [HB]/[B^-]$

Quantity	$B = 2$	$B = 1$	$B = 0.5$
k_p/k_{-1}	1·1	1·55	2·0
k_0/k_{-1}	0·02	0·015	0·01

TABLE V

Values of the activation energy E_a (kJ mol^{-1}) and activation entropy $\Delta S^{\ddagger}$ (J K^{-1} mol^{-1}) of compounds *IIIa* and *IIIc — IIIf* solvolyzed in 1 : 1 acetate buffer with ionic strength 1 mol l^{-1}

Quantity	*IIIa*	*IIIc*	*IIIe*	*IIId*	*IIIf*
E_a	89·5	116	110	70	82
$\Delta S^{\ddagger}$	−67	6	7·6	−70·6	−61·5

nitrogen of CH_3N group of the intermediate In is more basic than that in compound IIId, since its free electron pair is not involved in conjugation and, moreover, the polar N—S bond was split.
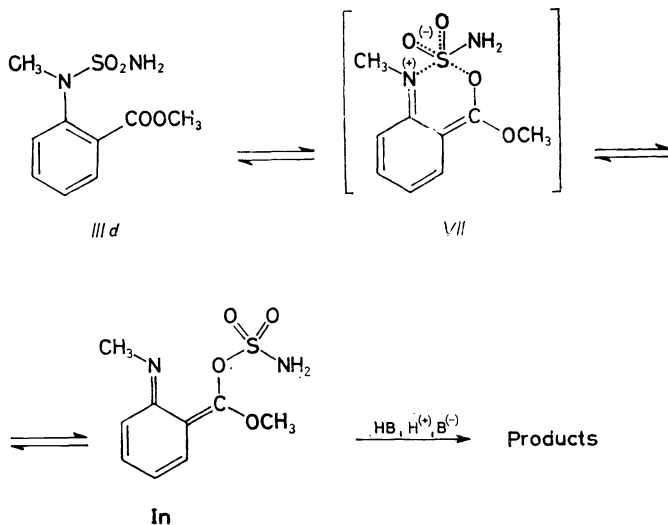
SCHEME 7

The value of Brönsted coefficient α determined from the dependence of $\log k_{BH}/k_{-1}$ vs pK of the acid in methanol[24] is 0·8 to 0·9, hence close to 1, which means that the proton transfer from the acidic buffer component to the intermediate is considerably unfavourable thermodynamically[24].

Protonated methanol is a stronger acid than dichloroacetic acid by 8 orders of magnitude. The rate constant k_{BH} can be presumed to approach the rate constant of the diffusion-controlled protonation of an amine $(k \sim 2 . 10^{10} \, 1 \, mol^{-1} \, s^{-1}$, ref.[25]). As the methanolysis rate coefficient k_{obs} does not decrease even at $[H^+] = 2·5 .$ $. 10^{-3} \, mol \, l^{-1}$, it must be $k_H > 10^4 k_{-1}$, hence $k_{-1} < 10^6 \, s^{-1}$. Thus the intermediate In has a relatively fairly long lifetime.

Although bromine as a substituent can, by its free electron pair, relatively efficiently stabilize electron-deficient centres[26], its anchimeric effect in the methanolysis of compound IIIf is smaller than the effect of methoxycarbonyl group in compound IIId, and the stability of an intermediate similar to In in Schemes 6 and 7 is lower in the case of compound IIIf. In accordance therewith, the intermediate from compound IIIf is formed (k_1) more slowly by about 2·5 orders of magnitude. If it is presumed that $k_H \sim 2 . 10^{10} \, 1 \, mol^{-1} \, s^{-1}$, then $k_{-1} = k_H/33 \sim 6 . 10^8 \, s^{-1}$. Hence the decomposition of the intermediate from compound IIIf is faster than in the case of

the 2-methoxycarbonyl derivative *IIId* by more than 2 orders of magnitude. The result of lower stability of intermediate from *IIIf* is a higher acidity of the proton of NH_2 group and higher basicity of the nitrogen of methylamino group. So the rate constants of transformation of this intermediate into products (k_{BH} and k_B for the catalyses by acetic acid and acetate ion, respectively) are 2–3 orders higher for compound *IIIf* than for *IIId**.

It seems very likely that with respect to the far lower stabilization of the leaving group $\overset{(+)}{SO_2NH_2}$ by bromine atom (as compared with the stabilization by *o*-methoxy-carbonyl group) the proton transfer to acetate ion represents a diffusion-controlled reaction, too.

Effects of Solvent and of the Presence of N-Methyl Group
on Solvolyses of Sulfuric Diamides

From data of Table I it is obvious that the rate constants k_0 of solvolyses of compounds *IIIa* and *IIIb* are smaller in water than in methanol by a factor of 10, whereas the respective factor for k_A at the same conditions is less than 2. The solvent effect on the solvolysis rate of compound *IIId* is seen in Table VI. With increasing content of water in its mixtures with methanol, the value of $k_{obs} = k_1$ rapidly decreases. The change in k_{obs} is not caused by a change in relative permittivity of the solvent, since additions of other solvents with lower relative permittivities as compared with

TABLE VI
The observed rate coefficients k_{obs} (s^{-1}) of the hydrochloric-acid-catalyzed solvolysis of compound *IIId* in methanolic solutions (vol. %) of water (W), 1-butanol (B), and tetrahydrofuran (T) at 25°C at the ionic strength of 0·125 mol l^{-1}

W	$k_{obs} \cdot 10^4$	B	$k_{obs} \cdot 10^4$	T	$k_{obs} \cdot 10^4$
0	19·00	50	9·3[b]	50	12·8[b]
25	5·25	50	14·8[c]	50	18·6[c]
50	2·50	100	5·2[b]		
75	1·28	100	8·75[c]		
100	0·83	—	—		

$c_{HCl} =$ [a] 0·01; [b] 0·001; [c] 0·005 mol l^{-1}.

*   The kinetic measurements in both buffers and methanolic HCl were carried out at 25°C with compound *IIId* and at 70°C with compound *IIIf*. The rate constants k_{-1}, k_H, k_B, k_{HB} of the reactions of intermediate are large, hence the respective activation energies must be very small and, hence, also the effect of temperature on the rates of these reactions must be small.

methanol (1-butanol, tetrahydrofuran) have small influence on the solvolysis rates (Table VI). The main reason of the large decrease in k_{obs} observed with increasing water content consists obviously in the fact that water − in contrast to other solvents − strongly solvates the polar sulfamoyl group of the starting compound, whereas the difference in solvation of the activated complex by various solvents is far less. The effect of water on the rate constants k_0 of solvolyses of compounds *IIIa* and *IIIb* probably can be explained in similar way.

If the methyl group at nitrogen is replaced by hydrogen, k_{obs} is lowered by more than 2 orders of magnitude irrespective of the solvolysis mechanism. Table V presents the activation energies and entropies of compounds *IIIa, IIIc, IIId, IIIe*, and *IIIf*. The large retardation of the solvolyses of the compounds not containing N-methyl group (*IIIc, IIIe*) is a consequence of greater value of the activation energy. The values of $\Delta S^{\ne}$ are noteworthy. The derivatives containing N-methyl group have $\Delta S^{\ne} = -60$ to -70 J K^{-1} mol^{-1}, whereas the derivatives without N-methyl group exhibit positive $\Delta S^{\ne}$ values which are, within experimental error, practically the same in spite of the fact that the reactions go by different mechanisms. Compounds *IIIa* and *IIIc* are solvolyzed by the addition elimination mechanism, the solvolysis of the dibromo derivative *IIIf* involves the predominantly acetate-ion-catalyzed decomposition of the intermediate as the rate-limiting step, and the formation of unstable intermediate is rate limiting in the case of compounds *IIId* and *IIIe*. The decisive factor obviously is the solvation of the NH group in phenylamino group which causes a lowering in the energy of initial state and, hence, an increase in the activation energy and the therewith connected large drop in the entropy of the initial state; thus $\Delta S^{\ne}$ has a positive value.

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