Tetrahedron. Vol. 25, pp. 5655 to 5667. Pergamon Press 1969. Printed in Great Britain

SYNTHESIS AND SOLVOLYSIS OF COVALENT SULFONYLMETHYLPERCHLORATES

A. BRUGGINK, B. ZWANENBURG and J. B. F. N. ENGBERTS
Department of Organic Chemistry, the University, Bloemsingel 10, Groningen, The Netherlands

(*Received in the UK* 11 *July* 1969; *Accepted for publication* 4 *August* 1969)

Abstract—Six representatives (Ia–If) of a new class of covalent perchlorates, i.e. alkyl- and arylsulfonylmethylperchlorates have been prepared from the corresponding α-diazosulfones and perchloric acid in an aprotic solvent. The compounds show a remarkable thermal stability, but are sensitive to shock. Hydrolysis of these perchlorates gives the parent sulfinic acid, formic acid and chloric acid. It is a kinetically general base-catalysed reaction as indicated by rate measurements in buffer solutions, solvent deuterium isotope effects and the absence of CH/CD exchange during solvolysis. The Brønsted coefficient for Ia, the activation parameters and the substituent effect on the rates of hydrolysis are discussed in terms of the proposed mechanism. In the fast product determining steps a redox reaction is involved, in which possibly an α-oxosulfone is intermediate.

INTRODUCTION

ALTHOUGH ionic perchlorates have been studied extensively,[1] their organic covalent counterparts[1–3] have received much less attention, presumably because of their extremely explosive properties. However, recently we reported[4] the synthesis of two representatives of a new class of covalent perchlorates, i.e. sulfonylmethylperchlorates (Ia, R = p-$CH_3C_6H_4$; Ib, R = $C_6H_5CH_2$), which could be isolated in an analytically pure state. These compounds can be handled safely in small quantities, but they detonate violently when struck with a hammer. Their formation from an α-diazosulfone[5] and concentrated perchloric acid in an aprotic solvent has been discussed[4] and involves the perchlorate anion as a nucleophile. The synthesis of several new sulfonylmethylperchlorates and a discussion of their PMR and IR spectral data are reported in this paper.

$$RSO_2CHN_2 + HClO_4 \rightarrow RSO_2CH_2OClO_3 + N_2$$

In a preliminary communication[6] we reported that the hydrolysis of Ia and Ib was subjected to general base catalysis. The kinetics of the hydrolysis reaction have now been studied in more detail and a more definite picture of the mechanistic pathway has been obtained.

SYNTHESIS

Four new covalent sulfonylmethylperchlorates (Ic, R = C_6H_5; Id, R = p-ClC_6H_4; Ie, R = m-ClC_6H_4; If, R = p-$NO_2C_6H_4$) were prepared by essentially the same procedure as reported earlier[4] for Ia and Ib. In most cases the yields of pure compounds were below 50% because considerable amounts of material were lost due to hydrolysis of the α-diazosulfones[4] and the sulfonylmethylperchlorates in the reaction mixture. Also recrystallization caused a substantial drop in the yield.

The structure of the sulfonylmethylperchlorates is based on correct elemental

TABLE. 1. THE SULFONYLMETHYLPERCHLORATES, $RSO_2CH_2OClO_3$

			IR data, Perkin Elmer 125, 10 mg/ml CCl_4		PMR data, δ (ppm); Concn 0·02 M			
Compound	Yield	M.p. °C.	ν_{OClO_3} ($\pm 2\ cm^{-1}$)	ν_{SO_2} ($\pm 2\ cm^{-1}$)	$SO_2CH_2OClO_3$		Phenyl protons	Other groups
					$CDCl_3$‡	C_6D_6‡	$CDCl_3$	$CDCl_3$
Ia * R = p-$CH_3C_6H_4$	49	92–94	1246 (m) 984 (m) 1266 (w) 1281 (m)	1158 (s) 1300 (sh) 1352 (s)	5·284 (s)	4·520 (s)	7·30–7·88 (A_2B_2)	2·49 (s) p-CH_3
Ib * R = $C_6H_5CH_2$	44	120·5–121·5	1248 (m) 984 (m) 1266 (w) 1282 (m)	1151 (m) 1300 (sh) 1354 (s)	5·050 (s)	4·220 (s)	7·43 (s)	4·37 (s) $C_6H_5\underline{CH_2}$-
Ic R = C_6H_5	52	94–95	1246 (m) 985 (m) 1265 (w) 1282 (m)	1159 (s) 1298 (sh) 1354 (s)	5·308 (s)	4·475 (s)	7·6–8·1 (m)	
Id R = p-ClC_6H_4	31	73·74	1246 (m) 986 (m) 1266 (w) 1282 (m)	1160 (s) 1300 (sh) 1356 (s)	5·321 (s)	4·391 (s)	7·49–7·95 (A_2B_2)	
Ie R = m-ClC_6H_4	32	66–67·5	1246 (m) 986 (m) 1266 (w) 1282 (m)	1160 (s) 1294 (sh) 1357 (s)	5·335 (s)	4·305 (s)	7·52–7·93 (m)	
If R = p-$NO_2C_6H_4$	14	105–106	1249 (m) 989 (m) 1284 (m)†	1159 (s) 1309 (w) 1346 (s)†	5·400 (s)	4·343 (s)	8·08–8·55 (A_2B_2)	

* Yield and melting point taken from Ref. 4.

† In $CHCl_3$, 20 mg/ml s = strong, m = medium, w = weak, sh = shoulder.

‡ Estimated accuracy: ±0·004 ppm. Recorded on Varian A-60 using an audio oscillator side band technique. s = singlet, m = multiplet.

analyses and PMR and IR spectral data (Table 1). The low field PMR signals at about $\delta = 5{\cdot}2$ ppm in $CDCl_3$ are characteristic for methylene protons flanked by two electronegative groups.

The IR absorption at about 1260 cm^{-1} (triplet) is ascribed to the asymmetric stretching vibration of the Cl—O* group in $RSO_2CH_2O^*ClO_3$, by analogy with *n*-alkylperchlorates.[7] The corresponding symmetric stretching vibration is probably found at about 985 cm^{-1}. In all cases an absorption at about 1100 cm^{-1}, which is characteristic for the perchlorate anion,[8] is absent. Also in accordance with the proposed covalent structure is the good solubility of Ia-If in non-polar solvents like benzene and dichloromethane.

The perchlorate esters can be handled safely in small quantities; however they detonate violently when struck with a hammer.

SOLVOLYSIS: RESULTS AND DISCUSSION

Reaction products. Hydrolysis of Ia in 0·10N NaOH and subsequent acidification afforded *p*-toluenesulfinic acid (yield 60%) which was identical with an authentic sample (mixed m.p., IR and PMR spectra). The previously reported[6] resorcinol test which would indicate the presence of formaldehyde was found to be unreliable in the presence of sulfinic acid. PMR spectra of the reaction mixtures obtained after complete hydrolysis of Ia, Ic and Id revealed the quantitative formation of *formic acid* ($\delta_{HCOOH} = 8{\cdot}18$ ppm in 50% (v/v) dioxan-D_2O). Under a variety of conditions (0·1N NaOH; water; 0·01N NaOH at concentrations of Ia which were also used in the kinetic experiments) *chloric acid* was shown to be the third product of hydrolysis by a positive and reproducible test with manganous sulfate and polyphosphoric acid.[9]*

The quantitative formation of the corresponding sulfinic acids upon hydrolysis of Ia–If in water, dilute aqueous perchloric acid and 0·1N NaOH was indicated by the fact that the UV spectra of the reaction mixtures after complete hydrolysis were identical within 4% with those of the authentic sulfinic acids in the same media. Methanolysis of Ia with sodium methoxide in methanol gave sodium *p*-toluenesulfinate in 95% yield.

Kinetic measurements. The rates of hydrolysis of the covalent sulfonylmethylperchlorates Ia-If could easily be determined by following the change in the UV spectra as a function of time. Pseudo first order kinetics were found for at least three half lifes. Because of the strong catalysis by bases (*vide infra*), the rates of hydrolysis could be measured conveniently at 25° only at a rather low pH (< 6).

Base catalysis vs *nucleophilic displacement.* Extensive evidence[10] exists that the perchlorate anion is a very weak nucleophile and therefore a good leaving group in nucleophilic displacements reactions. However, rate determining nucleophilic displacement of ClO_4 in Ia–If could be excluded definitely as shown by measurements of the rate of hydrolysis in the presence of halide ions. The addition of substantial amounts of the strongly nucleophilic bromide ions results in a *decrease* in rate (Tables 2 and 3). No sulfonylmethylhalides were formed since the UV spectra of the reaction mixtures showed only the presence of the corresponding sulfinic acids.

Rate measurements in aqueous carboxylic acid-sodium carboxylate buffers

---

* Perchloric acid, *p*-toluenesulfinic acid, formic acid and formaldehyde, or mixtures of these compounds, did not interfere with these tests for chloric acid.

showed that the hydrolysis reaction was strongly catalyzed by base. The constant value of k_ψ in the acidity range of 0·01–0·1N $HClO_4$ (Table 2) excludes acid catalysis for the hydrolysis reaction. In order to decide between specific and general base catalysis the following criteria were applied: buffer and water contribution, solvent deuterium isotope effect and H-D exchange at the reaction center.

Buffer and water contribution. Rate measurements were carried out for Ia in acetic acid-sodium acetate buffer solutions with different total concentration but a constant acid/base ratio and a constant ionic strength μ. The results are given in Table 3 and Fig. 1 Reaction rates varied linearly with the concentration of acetate ions indicating *general base catalysis*: rate $= k_\psi \cdot c_I = (k_{OH^\ominus} \cdot c_{OH^\ominus} + k_{AcO^\ominus} \cdot c_{AcO^\ominus} + k_{H_2O} \cdot c_{H_2O}) c_I$. From a plot of k_ψ *vs* $c_{AcO}\theta$ values for $k_{AcO^\ominus}$ and for $k_{OH^\ominus} \cdot c_{OH^\ominus} + k_{H_2O}$ were obtained (Fig. 1). The constant value of the term $k_{OH^\ominus} \cdot c_{OH^\ominus} + k_{H_2O} \cdot c_{H_2O}$ in the pH range

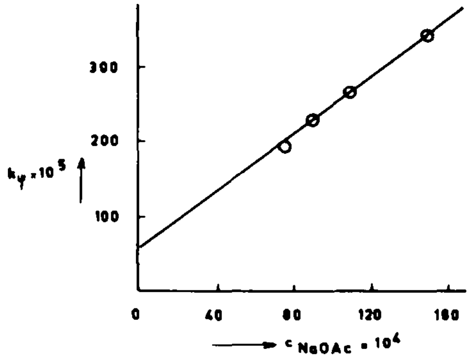


FIG. 1 Second order rate constant for the hydrolysis of Ia in acetic acid–sodium acetate buffer solution (μ = 0·100 N) at 25° (pH = 4·86).

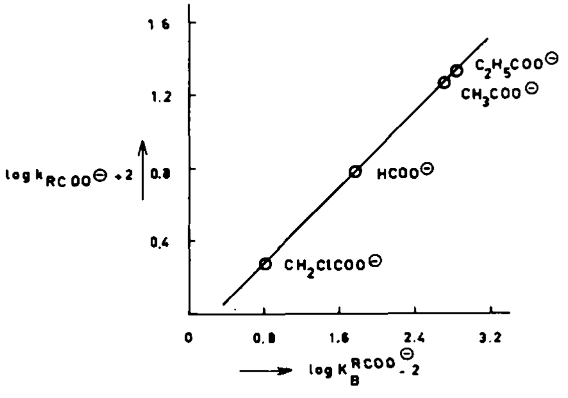


FIG. 2 Brønsted plot for the hydrolysis of Ia.

3·8–4·9 shows that the contribution of hydroxide ions to the reaction rate is negligible in these media. Consequently $k_{H_2O} \cdot c_{H_2O}$ amounts to 54. 10^{-5} sec^{-1}. This value is in excellent agreement with the rate constant for Ia in 0·01–0·10 N $HClO_4$ (Table 2) where water is the only base present. The buffer contribution for the base catalyzed

TABLE 2. PSEUDO FIRST ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF Ia–If IN AQUEOUS (H_2O OR D_2O) $HClO_4$ (μ = 0·10 N) AT 25°

Compound in	UV* (mμ)	$c_{HClO_4} \cdot 10^4$ (mole. l^{-1})	$c_{NaClO_4} \cdot 10^4$ (mole. l^{-1})	$c_{NaBr} \cdot 10^4$ (mole. l^{-1})	pH	$k_\psi \cdot 10^5$ (sec.$^{-1}$)	k_{H_2O}/k_{D_2O}
Ia in H_2O	230	971				55·5	
Ia in H_2O		491	500			54·9	
Ia in H_2O†		938		5000		43·7	
Ia in H_2O†		952	5000			45·0	
Ia in D_2O		500	500		1·45	32·8	1·70
Ib in H_2O	230	65	935			61·5	
Ib in H_2O		170	830			60·6	
Ib in H_2O		616	385			61·1	
Ib in H_2O†		1923				58·3	
Ib in H_2O†		3814				56·8	
Ib in H_2O†		4344				53·6	
Ib in H_2O†		947		5000		45·2	
Ib in H_2O†		947	10,000			44·8	
Ib in D_2O		600	400		1·20	29·8	2·06
Ic in H_2O	225	938				74·1	
Ic in H_2O		491	500			72·8	
Ic in H_2O		99	900			74·3	
Ic in D_2O		500	500		1·34	40·9	1·81
Id in H_2O	238	954				106·5	
Id in H_2O		491	500			110·0	
Id in H_2O		99	900			101·0	
Id in D_2O		500	500		1·38	58·5	1·82
Ie in H_2O	230	952				138·0	
Ie in H_2O		479	500			138·0	
Ie in H_2O		96	900			135·5	
Ie in D_2O		500	500		1·42	78·6	1·75
If in H_2O	235	939				311	
If in H_2O		500	500			313	
If in H_2O		91	900			307	
If in D_2O		500	500		1·46	172	1·80

* Wavelength in UV spectrum used for rate measurements.

† Ionic strength $\mu > 0·1$ N.

hydrolysis of If was evaluated using aqueous chloroacetic acid-sodium chloroacetate buffer solutions (Table 4). In the pH range 2·2–2·8 the concentration of hydroxide ions is again too low to contribute to the reaction rate. The contribution of water as the general base is in agreement with that found in dilute perchloric acid (Table 2).

Brønsted equation. For four carboxylate anions the contribution to the reaction rate of Ia was determined (Table 3). A straight line was obtained by plotting log $k_{RCOO^\ominus}$ *vs* log $K_B^{RCOO^\ominus}$, being the basicity constant of the carboxylate anion (Fig. 2). The β value of the Brønsted relation[11] log $k_{RCOO^\ominus} = \alpha + \beta \log K_B^{RCOO^\ominus}$ amounts to 0·51, which may be interpreted as an indication for a relatively incomplete proton transfer in the rate determining step.[12, 13]

The solvent deuterium isotope effect. The solvent deuterium isotope effect k_{H_2O}/k_{D_2O} can be used to differentiate between specific and general base catalysis.[14] In the former

TABLE 3. RATE CONSTANTS FOR THE HYDROLYSIS OF Ia IN AQUEOUS CARBOXYLIC ACID-SODIUM CARBOXYLATE (RCOOH-RCOONa) BUFFERS ($\mu = 0{\cdot}100$N) AT 25°.

R	$c_{RCOOH} \cdot 10^4$ (mole.l^{-1})	$c_{RCOONa} \cdot 10^4$ (mole.l^{-1})	$c_{NaCl} \cdot 10^4$ (mole.l^{-1})	$c_{NaBr} \cdot 10^4$ (mole.l^{-1})	pH	$k_\psi . 10^5$ (sec^{-1})	$k_{RCOO^\ominus} . 10^3$* (l.mole^{-1}.sec^{-1})	$(k_{OH^\ominus} . c_{OH^\ominus} + k_{H_2O} . c_{H_2O})$* $. 10^5$ (sec^{-1})
Me	563	63	937		3·76	178	196	54
	450	50	950		3·77	148		
	338	28	962		3·78	127		
	225	25	975		3·77	103		
Me	350	150	850		4·32	338	193	54
	315	135	865		4·31	312		
	265	110	890		4·32	261		
	175	75	925		4·31	194		
Me	100	150	850		4·85	340	194	55
	75	110	890		4·85	263		
	60	90	910		4·86	230		
	50	75	925		4·86	196		
Me	100	150	100	5000†	4·78	305		
H	50	200	800		4·14	176	60·2	53
	100	150	850		3·69	145		
Et	150	100	900		4·53	270	215	56
	100	150	850		4·88	378		
CH_2Cl	50	200	800		3·31	94·2	19·6	54
	25	225	775		3·69	99·2		

* Obtained from the plot of k_ψ *vs.* c_{RCOONa}.

† Ionic strength $\mu > 0{\cdot}1$ N.

case k_{H_2O}/k_{D_2O} is smaller than unity, as found in numerous reactions following this mechanistic pathway.[14, 15] For generally base catalyzed reactions k_{H_2O}/k_{D_2O} should be larger than unity although little reliable evidence is available.[14, 15]

The solvent deuterium isotope effect has been determined for Ia–If in dilute perchloric acid solutions in which water is the general base. The ratio k_{H_2O}/k_{D_2O} for the arylsulfonylmethylperchlorates is in the range of 1·7–1·8 and for benzylsulfonylmethylperchlorate it amounts to 2·1 (Table 2). Rate measurements on Ia in acetic-acid sodium acetate buffers in H_2O and D_2O respectively showed that there was no isotope effect on the buffer contribution. This is in accordance with the proposed general base catalysis.

H-D exchange in the substrate was tested by following the hydrolysis of Ia and Ib (in 5% D_2O-acetone-d_6) and Id (in methanol-d) by means of PMR spectroscopy. The spectral changes indicated the formation of sulfinic acid and formic acid (with D_2O) or methyl formate (with MeOD). Careful integration of the signals of substrate and products showed the absence of H-D exchange in the SO_2CH_2 moiety of the perchlorate.

Activation parameters. The activation parameters $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were determined for the hydrolysis of Ia and If in dilute perchlorate acid solutions from the rate constants measured at two different temperatures (Table 5). As pointed out by Laidler[16] the small negative entropy of activation of about −10 e.u. may be indicative for a transition state in which only little separation of charge has occurred.

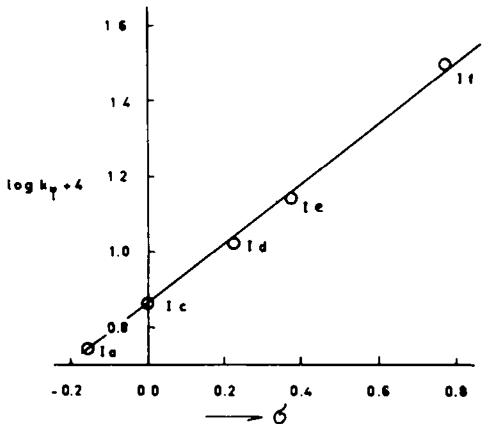


Fig. 3 Relation between Hammett σ and log k_ψ for the hydrolysis of arylsulfonylmethylperchlorates in dilute solutions of perchloric acid at 25°.

Substituent effects. The rates of five *p*- and *m*-substituted phenylsulfonylmethylperchlorates in dilute solutions of perchloric acid (Table 2) are correlated by Hammett's σ constants[17, 18] (Fig. 3). The small value of ρ (0·79) is in accordance with a partial proton transfer in the rate determining step. No deviation for If is observed, indicating the absence of direct resonance interaction between the *p*-nitro substituent and the partially negatively charged reaction site.

TABLE 4. RATE CONSTANTS FOR THE HYDROLYSIS OF If IN AQUEOUS CHLOROACETIC ACID-SODIUM CHLOROACETATE BUFFER SOLUTIONS (μ = 0·10N) AT 25°.

$c_{CH_2ClCOOH}\cdot10^4$ (mole·l^{-1})	$c_{CH_2ClCOONa}\cdot10^4$ (mole·l^{-1})	$c_{NaCl}\cdot10^4$ (mole·l^{-1})	pH	$k_\psi\cdot10^5$ (sec^{-1})	$k_{CH_2ClCOO^\ominus}\cdot10^{3}$* (l·mole^{-1}·sec^{-1})	$(k_{OH^\ominus}\cdot c_{OH^\ominus}+k_{H_2O}\cdot c_{H_2O})$* $\cdot10^5$(sec^{-1})
386	114	950	2·20	445	124	301
284	92	962	2·24	411		
185	66	975	2·28	380		
82	43	986	2·45	352		
207	143	860	2·57	482	119	314
136	114	900	2·65	452		
63	63	950	2·73	390		
48	52	960	2·76	375		

* Obtained from the plot of k_ψ *vs.* $c_{CH_2ClCOONa}$.

TABLE 5. PSEUDO FIRST ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF Ia AND If IN DILUTE PERCHLORIC ACID (μ = 0·10N) AT DIFFERENT TEMPERATURES.

Compound	$c_{HClO_4}\cdot10^4$ (mole·l^{-1})	Temp. (°K)	$k_\psi\cdot10^5$ (sec^{-1})	$\Delta G^\ddagger$ (Kcal·mole^{-1})	$\Delta H^\ddagger$ (Kcal·mole^{-1})	$\Delta S^\ddagger$ (e.u.)
Ia	938	312·0	235	21·9 ± 0·8	18·8 ± 0·4	− 10 ± 2
	971	298·2	55·5			
If	938	312·1	1201	20·9 ± 0·9	17·1 ± 0·5	− 13 ± 2
	939	298·2	311			

A straight line is obtained when log k_ψ for the hydrolysis of Ia–If in dilute solutions of perchloric acid is plotted *vs* the chemical shift of the methylene protons in deuterochloroform or in hexadeuterobenzene (Fig. 4).[*] The chemical shift of the methylene protons depends mainly on the polarization of the C—H bond. Since the rate of proton abstraction is also dependent on this C—H polarization such a linear relationship could be expected. The considerable upfield shifts (0·8–1·0 ppm) of these methylene proton signals in benzene as compared to the shifts in $CDCl_3$ are caused by interaction of the aromatic solvent with the strongly polarized C—H bonds.[19]

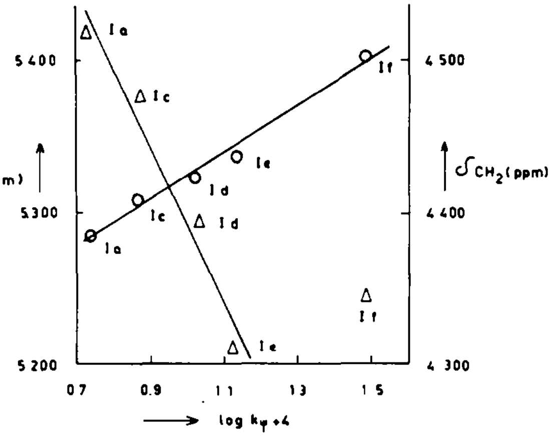


FIG. 4 Correlation between the chemical shift of the methylene protons in $CDCl_3$ (O) and in C_6D_6 (Δ) and the rate of hydrolysis in dilute solutions of perchloric acid.

Discussion of the mechanism. The data presented above show that the hydrolysis of the covalent sulfonylmethylperchlorates is subjected to general base catalysis which implies a rate determining proton transfer to a general base.[†] Upon proton removal in the rate controlling step an α-sulfonylcarbanion, $RSO_2CHOClO_3$, may be formed, followed by rapid product determining steps or the state of the carbanion may be bypassed in a concerted pathway.

Hence, nucleophilic displacement of the perchlorate group does not take place. This contrasts with the solvolysis of simple alkylperchlorates which show S_N2-type decomposition.[3,20] The formation of chloric acid as well as that of sodium *p*-toluenesulfinate upon methanolysis excludes α-elimination of perchloric acid to give an α-sulfonylcarbene. In the latter case one would expect the production of $RSO_2CH_2OCH_3$ from the carbene.[21]

Taking into account the relatively high acidity of the $—SO_2CH_2OClO_3$ moiety together with the Brønsted coefficient ($\beta = 0{\cdot}51$), the small negative entropy of activation ($\Delta S^\ddagger = -10$—-13 e.u.) and probably also the solvent deuterium isotope effect and the rather small ρ-value ($\rho = 0{\cdot}79$), it may be concluded that deprotonation

---

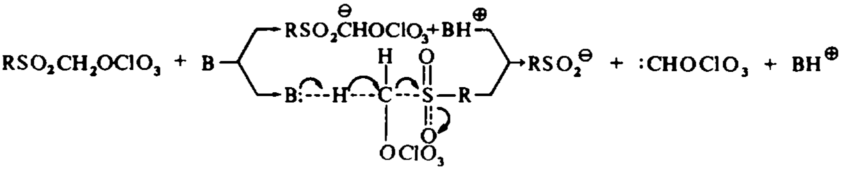
[*] The relatively low shielding of the methylene protons of If in C_6D_6 may be the result of a specific interaction of the strongly electrondeficient aromatic ring with benzene.

[†] Usually deprotonation next to a sulfonyl group is a specifically base catalysed process.[22,23]

has proceeded to a relatively small extent in the rate determining step. Although this evidence is not sufficient to decide between a carbanion-like and a concerted pathway, in view of the generally very high rates of protonation of α-sulfonylcarbanions[22,23] it seems reasonable to assume a concerted mechanism.

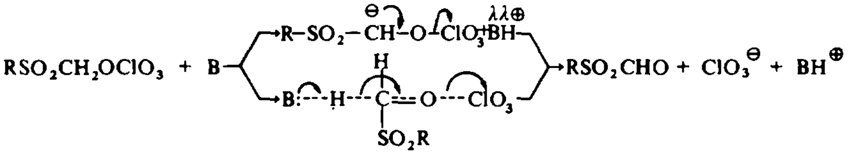
Two pathways are conceivable for the formation of the observed reaction products. Firstly, an α-elimination of sulfinate anion, either stepwise or concerted (see scheme α), which will give the carbene: $CHOClO_3$. On further hydrolysis this carbene should lead to formic acid and chloric acid.

SCHEME α:



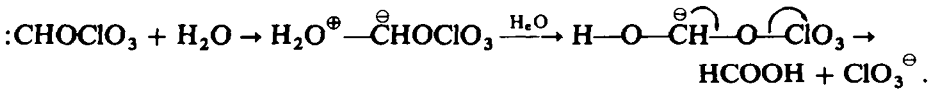
Secondly, a type of β-elimination may be operative in which chlorate anion is eliminated (see scheme β). This redox reaction results in the formation of an α-oxosulfone which is supposed to hydrolyse to formic acid and sulfinic acid.

SCHEME β



No experimental evidence in favour of one of the two schemes presented above has thus far been obtained. Attempts to trap the carbene, :$CHOClO_3$, or to detect the α-oxosulfone, RSO_2CHO, spectroscopically, were all unsuccessful.

The carbene formation in path α formally resembles the reaction of dichloromethyl methyl ether with base which proceeds *via* methoxychloromethylene produced by α-elimination of the deprotonated substrate[24] formed in an irreversible process. The reaction of the carbene:$CHOClO_3$ with water may be depicted as:



$$:CHOClO_3 + H_2O \rightarrow H_2O^{\oplus}\text{—}\overset{\ominus}{C}HOClO_3 \xrightarrow{H_2O} H\text{—}O\text{—}\overset{\ominus}{C}H\text{—}O\text{—}ClO_3 \rightarrow HCOOH + ClO_3^{\ominus}.$$

Although this redox reaction is the only conceivable way in which the observed products can be explained, protonation of $HO\overset{\ominus}{C}HOClO_3$ to $HOCH_2OClO_3$ is more likely to occur. Since simple alkylperchlorates undergo S_N2-type reactions,[3, 20] the perchlorate $HOCH_2OClO_3$ will be prone to such a displacement rather than to a redox reaction. This argument makes α-elimination less likely, but does not rule out this pathway entirely.

The first step of scheme β finds some support in the literature. Base catalysed decomposition of the covalent perchlorate $CF_3CH_2OClO_3$ gives $NaClO_3$ while the organic residue is oxidized.[25] Examples of reduction of organic nitrates upon treatment with base are known,[26, 27] for instance the formation of benzaldehyde and nitrite anion from the reaction of benzylnitrate with base[27] (general base catalysis with a concerted reaction path).

The pivotal intermediate, the α-oxosulfone RSO_2CHO, has not been described in the literature. By analogy with α-oxosulfoxides[28] it might be assumed that α-oxosulfones will be very sensitive to nucleophilic reagents. Subsequent elimination of sulfinic acid will give the observed reaction products:

$$RSO_2CHO + H_2O \rightarrow RSO_2CH(OH)_2 \rightarrow RSO_2H + HCOOH.$$

The available evidence precludes a definite choice between the two mechanisms, however in our opinion pathway β should be preferred.

It is noteworthy that a redox reaction occurs with sulfonyl- or trifluoromethyl substituted methylperchlorates, while on the other hand simple alkylperchlorates and benzoylmethylperchlorates[29] undergo a nucleophilic displacement of the perchlorate group upon hydrolysis. This difference in reaction pattern may be correlated with the relative ease in which a halide atom attached to a RSO_2CH_2-, CF_3CH_2-, n-alkyl or $C_6H_5COCH_2$— group respectively can undergo a bimolecular displacement reaction.[30]

EXPERIMENTAL

Starting materials, solvents, reagents. The α-diazosulfones, RSO_2CHN_2, were prepared by the method of Van Leusen and Strating.[5, 31] The solvents dichloromethane and 1,2-dichloroethane were distilled from P_2O_5 before use. The water, used in the kinetic measurements, was demineralized and distilled twice in an all-quartz distillation unit. Deuterium oxide was obtained from "Reactor Centrum Nederland" (99·94% D_2O) and was used as such. Pro analyse grade materials were used for the preparation of the buffer solns.

M.ps were recorded on an electrically heated oil bath and are uncorrected. The elemental analyses were carried out in the micro-analytical department of the laboratory, directed by Mr. W. M. Hazenberg.

Synthesis of the covalent perchlorates Ia–If

General procedure. The α-diazosulfone (3 mmole) dissolved in 20 ml CH_2Cl_2 or 1,2-dichloroethane was placed in a 50 ml 3-necked flask fitted with a gasburette. At room temp 1·5–2·0 equivs of perchloric acid (70% soln in water) were added to the magnetically stirred soln. A brisk evolution of N_2 occurred and the yellow colour of the soln vanished. After a few min a nearly equimolar volume of N_2 had been evolved. The almost colourless soln was stirred for an additional 30 min. Then the reaction mixture was poured into 25 ml water and the resulting mixture was carefully neutralized with $NaHCO_3$ to pH 6–7. The water layer was extracted 3 times with 20 ml CH_2Cl_2. The combined organic layers were washed with 10 ml water and dried over $MgSO_4$. The solvent was removed *in vacuo* at 20° with a rotary evaporator. The crude product (usually a clear viscous oil, which solidified upon cooling at −30°) was purified by crystallization from ether/hexane or ether/light petroleum (40–60°).

N.B. Because of the explosive nature of the compounds all manipulations have to be carried out behind safety screens. It is strongly recommended to wear a safety cap and leather gloves when handling these covalent perchlorates.

p-*Tolylsulfonylmethylperchlorate,* (Ia) and *Benzylsulfonylmethylperchlorate,* (Ib). See Ref. 4.

Phenylsulfonylmethylperchlorate, (Ic). From 0·600 g (3·30 mmole) phenylsulfonyldiazomethane and 0·35 ml (4·0 mmole) perchloric acid 0·433 g (52%) of analytically pure Ic were obtained after two crystallizations from ether/light petroleum (40–60°). (Found: C, 33·7, 33·6; H, 3·1, 2·8; S, 12·7, 12·9. Calc. for $C_7H_7ClO_6S$: C, 33·02; H, 2·77; S, 12·59%).

p-*Chlorophenylsulfonylmethylperchlorate,* (Id). From 0·640 g (2·85 mmole) of *p*-chlorophenylsulfonyldiazomethane dissolved in 1,2-dichloroethane, and 0·30 ml (3·5 mmole) of perchloric acid 0·254 g (31%) of analytically pure Id were obtained after three crystallizations from ether/light petroleum (40–60°). (Found: C, 29·5, 28·9; H, 2·4, 2·3; S, 11·3, 11·6. Calc. for $C_7H_6Cl_2O_6S$: C, 29·05; H, 2·09; S, 11·09%). The elemental analysis of this compound was very troublesome, since some explosions occurred during the analysis.

m-*Chlorophenylsulfonylmethylperchlorate*, (Ie) was prepared from 0·610 g (2·81 mmole) *m*-chlorophenylsulfonyldiazomethane[31] dissolved in CH_2Cl_2, and 0·35 ml (4·0 mmole) perchloric acid. After two crystallizations from ether/light petroleum (40–60°) 0·254 g (32%) analytically pure Ie was obtained. (Found: C, 29·1, 29·4; H, 2·2, 2·2; S, 11·4, 11·4. Calc. for $C_7H_6Cl_2O_6S$: see Id).

p-*Nitrophenylsulfonylmethylperchlorate*, (If) was prepared from 0·500 g (2·20 mmole) *p*-nitrophenylsulfonyldiazomethane dissolved in 1,2-dichloroethane, and 0·30 ml (3·5 mmole) perchloric acid. Because of a slight impurity in the starting material the crude product (0·540 g) could not be purified by crystallization. After chromatography over silica with CH_2Cl_2 as the eluent (this caused a great loss of material) and one crystallization from ether/hexane 0·090 g (14%) analytically pure If was obtained. (Found: C, 28·2, 28·4; H, 1·9, 2·0; N, 4·6, 4·5. Calc. for $C_7H_6ClNO_8S$: C, 28·05; H, 2·02; N, 4·68%).

Reaction products. To 10 ml of 0·10N NaOH, 0·208 g (0·78 mmole) Ia dissolved in 10 ml dioxan were added while N_2 was passed over. Within 5 min the pH was below 6. After stirring for another 3 hr the reaction mixture was acidified with 2N H_2SO_4 to pH 0–1. The slightly turbid mixture was extracted with 4 portions 10 ml CH_2Cl_2. The water layer was acidified with 5 ml 2N H_2SO_4 and extracted again with 2 portions 10 ml CH_2Cl_2. The combined organic layers were washed with 10 ml 2N H_2SO_4 and dried over $MgSO_4$. The solvent was removed *in vacuo* at 20° giving 0·093 g (77%) of a white solid (m.p. 70–76°). After two crystallizations from ether/hexane 0·072 g (60%) pure *p*-toluenesulfinic acid was isolated, m.p. 79–84°, mixed m.p. 79–85°.

Methanolysis of Ia with NaOMe in MeOH was performed at room temp, in a N_2 atm and with the exclusion of moisture. Na (0·036 g, 1·58 mgrat was dissolved in 25 ml MeOH. After the addition of 0·198 g (0·74 mmole) Ia the soln was stirred for 4 hr. The MeOH was removed *in vacuo* and the resulting pale yellow solid was washed with 10 ml ether leaving 0·200 g of a white solid (m.p. >230° dec). The presence of chlorate anions appeared from the positive spot tests[9] with manganous sulfate and polyphosphoric acid while the IR and PMR (in D_2O) spectra indicated the presence of sodium *p*-toluenesulfinate (estimated yield 95%).

Kinetic measurements. The hydrolysis reactions were carried out in 2·0 cm quartz cells, equipped with a magnetic stirring device. The cells were placed in the adequately thermostated (±0·04°) cell compartment of a Zeiss P.M.Q. II spectrophotometer. About 1 mg of the perchlorate was dissolved in about 0·1 ml dry MeOH; 2 or 3 drops of this soln were added to the content of the cell. At intervals the absorbance was measured, during 3 half lifetimes. After 10 half lives the end absorbance was recorded. Pseudo first order rate constants, k_ψ, were obtained by plotting log $(E_t - E_\infty)$ *vs* time. The pseudo first order kinetics were found for at least 3 half lives. Rate constants were averaged over 2 measurements and were reproducible to within 3%. After each rate measurement the UV spectrum of the product of hydrolysis was recorded.

Acknowledgement—The authors are much indebted to Professor J. Strating for his stimulating interest.

REFERENCES

[1] J. C. Schumacher, *Perchlorates; Their Properties, Manufacture and Uses*, Reinhold, New York, N.Y. (1960).

[2] G. N. Dorofeenko, S. V. Krivun, V. I. Dulenko and Yu. A. Zhdanov, *Russ. Chem. Rev.* **34**, 88 (1965).

[3] H. Burton and P. F. G. Praill, *Analyst.* **80**, 4 (1955).

[4] J. B. F. N. Engberts and B. Zwanenburg, *Tetrahedron Letters* 831 (1967).

[5] A. M. van Leusen and J. Strating, *Rec. Trav. Chim.* **84**, 151 (1965).

[6] J. B. F. N. Engberts, A. Bruggink and B. Zwanenburg, *Tetrahedron Letters* 1265 (1968).

[7] J. Radell, J. W. Connolly and A. J. Raymond, *J. Am. Chem. Soc.* **83**, 3958 (1961).

[8] E. A. V. Ebsworth, *Infrared Spectroscopy and Molecular Structure* (Edited by M. Davies), p. 138. Elsevier, Amsterdam (1963).

[9] F. Feigl, *Spot Tests in Inorganic Analysis* (5th Edition) p. 297. Elsevier, Amsterdam (1958).

[10] R. E. Davis, *Survey of Progress in Chemistry* (Edited by A. F. Scott) Vol. 2; p. 189. Academic Press, New York (1964) and R. E. Davis, H. Nakshbendi and A. Ohno, *J. Org. Chem.* **31**, 2702 (1966). See also J. B. F. N. Engberts and B. Zwanenburg, *Tetrahedron* **24**, 1737 (1968).

[11] J. N. Brønsted and K. J. Pedersen, *Z. physik. Chem.* **108**, 185 (1924).

[12] R. P. Bell, *Acid-Base Catalysis* pp. 83, 159. Oxford University Press, London (1941).
[13] R. P. Bell, *The Proton in Chemistry* p. 155. Cornell University Press, Ithaca (1959).
[14] J. Hine, *Physical Organic Chemistry* (2nd Edition) p. 121. McGraw-Hill, New York, N.Y. (1962).
[15] F. A. Long and J. Bigeleisen, *Trans. Faraday Soc.* **55**, 2077 (1959).
[16] K. J. Laidler, *Reaction Kinetics, part II, Reactions in Solutions* p. 24. Pergamon Press, Oxford (1963).
[17] L. P. Hammett, *Physical Organic Chemistry.* McGraw-Hill, New York, N.Y. (1940).
[18] H. H. Jaffé, *Chem. Rev.* **53**, 191 (1953).
[19] T. Ledaal, *Tetrahedron Letters* 1683 (1968).
[20] J. Koskikallio, *Suomen Kemistilehti* B **40**, 131 (1967).
[21] R. J. Mulder, A. M. van Leusen and J. Strating, *Tetrahedron Letters* 3057 (1967).
[22] D. J. Cram, *Fundamentals of Carbanion Chemistry.* Academic Press, New York, N.Y. (1965).
[23] J. Weinstock, R. G. Pearson and F. G. Bordwell, *J. Am. Chem. Soc.* **78**, 3473 (1956).
[24] J. Hine, R. J. Roscup and D. C. Duffey, *Ibid.* **82**, 6120 (1960).
[25] C. E. Inman, E. A. Tyczkowski, R. E. Oesterling and F. L. Scott, *Experientia* **14**, 355 (1958).
[26] G. R. Lucas and L. P. Hammett, *J. Am. Chem. Soc.* **64**, 1928 (1942).
[27] E. Buncel and A. N. Bourns, *Canad. J. Chem.* **38**, 2457 (1960).
[28] T. Kumamoto and T. Mukaiyama, *Bull. Chem. Soc. Japan* **41**, 2111 (1968).
[29] B. Zwanenburg and N. F. Bosch, to be published.
[30] F. G. Bordwell and W. T. Brannen, *J. Am. Chem. Soc.* **86**, 4645 (1964).
[31] J. B. F. N. Engberts, G. Zuidema, B. Zwanenburg and J. Strating, *Rec. Trav. Chim.* **88**, 641 (1969).