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COVALENT SULFONYLMETHYLPERCHLORATES.

MECHANISM OF HYDROLYSIS

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Recently we described a new class of covalent perchlorates, i.e. sulfonylmethylperchlorates (I) (1), which could be isolated in an analytically pure state and which showed remarkable thermal stability.

$$RSO_2CHN_2 + HClO_4 \xrightarrow{ClCH_2CH_2Cl} RSO_2CH_2OClO_3 + N_2$$

Ia, R = $p\text{-}CH_3C_6H_4$
Ib, R = $C_6H_5CH_2$

Usually, covalent alkylperchlorates (2,3) are characterized and studied only with great difficulty because of their extremely explosive nature (4). They are known to hydrolyse rapidly (5), but no study of the mechanism has been published (6).

With the aim to elucidate the chemical behaviour of sulfonyl substituted methylperchlorates in solvolytic reactions, the mechanism of hydrolysis of p-tolylsulfonylmethylperchlorate (Ia) and benzylsulfonylmethylperchlorate (Ib) was investigated.

Hydrolysis of Ia in 0.10 N sodium hydroxide and subsequent acidification afforded after recrystallization, p-toluenesulfinic acid (in 60% yield) which was identical (IR, PMR, mixed melting point) with an authentic sample. The presence of formaldehyde in the reaction mixture was established by a positive resorcinol test.

Reaction mixtures obtained after hydrolysis of Ia and Ib in 0.10 N perchloric acid gave UV spectra identical with those of p-toluenesulfinic acid and benzylsulfinic acid respectively.

Pseudo first order rate constants k_ψ for the hydrolysis of Ia and Ib were obtained by following the absorbance at 230 mμ as a function of time. The solvolysis was strongly catalysed by bases such as hydroxide ion (in water) and methoxide ion (in methanol). Catalysis by acids was not observed since the same rate of hydrolysis was found in 0.04 N and 0.10 N perchloric acid. The rates of hydrolysis could be measured conveniently only at rather low pH.

Rate determining nucleophilic displacement is definitely excluded as shown by hydrolysis experiments in the presence of halide anions (Table I).

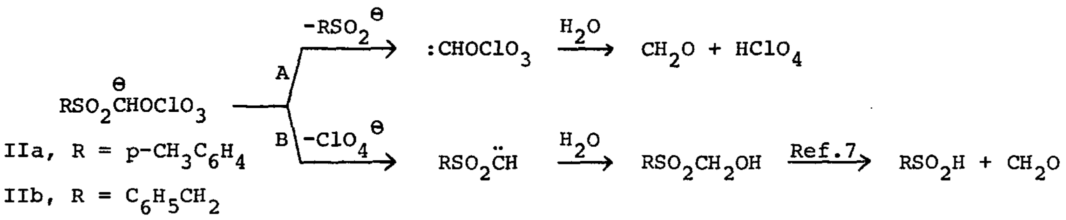
TABLE I

Rate constants of hydrolysis for Ia at 25^o in aqueous buffers with different halide anion concentrations.

pH	c_{AcOH} x 10^4 (mole. 1^{-1})	c_{NaOAc} x 10^4 (mole. 1^{-1})	c_{NaCl} x 10^4 (mole. 1^{-1})	c_{NaBr} x 10^4 (mole. 1^{-1})	k_ψ x10^3 (sec^{-1})
4.85	100	150	850		3.40
4.78	100	150	100	5000	3.05

The UV spectra of the reaction mixtures obtained after hydrolysis of Ia and Ib in aqueous buffers or perchloric acid with appreciable (0.5 N - 1.8 N) quantities of halide anions revealed that both compounds hydrolysed to the parent sulfinic acid. In no case sulfonylmethylhalides were detected.

These observations can be explained by assuming the intermediacy of a deprotonated substrate II. Elimination of either sulfinate anion or perchlorate anion from II may account for the observed products of hydrolysis as is illustrated in the following scheme.



Methanolysis of Ia with sodium methoxide in methanol gave a 90% yield of sodium p-toluenesulfinate (identified by its IR and PMR spectrum). The product expected according to route B, e.g. $p\text{-}CH_3C_6H_4SO_2CH_2OCH_3$, was not found (8). The UV spectrum of the product of solvolysis of Ia in pure methanol was identical with the spectrum of the parent sulfinic acid taken under the same conditions. These results can be reconciled only if the sulfinate anion is the leaving group (route A).

The solvent deuterium isotope effect of k_H/k_D = 1.7 for Ia in perchloric acid-sodium perchlorate solutions (μ = 0.100 N) at pH 1.45 and k_H/k_D =2.0 for Ib at pH 1.20 are indicative (9) of general base catalysis with water as a base.

This conclusion was confirmed for Ia by rate measurements in acetic acid-sodium acetate buffer solutions with different total concentration but a constant acid/base ratio and a constant ionic strength μ. The reaction rates varied linearly with the concentration of acetate ions. In these media k_ψ equals $k_{OH^\ominus}\cdot c_{OH^\ominus} + k_{AcO^\ominus}\cdot c_{AcO^\ominus} + k_{H_2O}\cdot c_{H_2O}$ and the second order rate constants can be evaluated (Table II).

TABLE II

Second order rate constants* for the hydrolysis of Ia in acetic acid-sodium acetate buffers (μ = 0.100 N) at 25°.

pH	$k_{AcO^\ominus} \times 10^3$ (1. mole.$^{-1}$ sec^{-1})	$(k_{OH^\ominus}\cdot c_{OH^\ominus} + k_{H_2O}\cdot c_{H_2O}) \times 10^3$ (sec^{-1})
3.77	196	0.54
4.32	193	0.54
4.85	194	0.55

* Obtained from the plot of k_ψ vs. $c_{AcO^\ominus}$

The constant value of the term $k_{OH^\ominus} \cdot c_{OH^\ominus} + k_{H_2O} \cdot c_{H_2O}$ in the pH range 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 0.54×10^{-3} sec^{-1}. This value is in excellent agreement with the rate constant for Ia found in 0.04 - 0.10 N perchloric acid ($k_\psi = 0.55 \times 10^{-3}$ sec^{-1}).

These data are consistent with rate determining proton transfer from the covalent sulfonylmethylperchlorate I to a general base B, yielding the carbanion II.

$$\underset{\text{I}}{RSO_2CH_2OClO_3} + B \xrightarrow{\text{slow}} \underset{\text{II}}{RSO_2\overset{\ominus}{C}HOClO_3} + HB^\oplus$$

In a subsequent fast step a sulfinate anion is eliminated from II, with the possible formation (10) of the carbene III, which on further hydrolysis will be converted to formaldehyde and perchloric acid.

$$\underset{\text{II}}{RSO_2\overset{\ominus}{C}HOClO_3} \xrightarrow{\text{fast}} RSO_2^\ominus + \underset{\text{III}}{:CHOClO_3}$$

$$\underset{\text{III}}{:CHOClO_3} + H_2O \xrightarrow{\text{fast}} CH_2O + HClO_4$$

A mechanism in which attack of the general base on I and elimination of the sulfinate anion is a concerted process (11) cannot be excluded, although the rather large solvent deuterium isotope effect favours the intermediacy of a free carbanion.

Details of this work together with an extension to other covalent perchlorates will be published in due time.

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