

MECHANISM OF REACTIONS OF α -DIAZOSULFONES—III¹

FURTHER STUDY OF THE ACID-CATALYSED HYDROLYSIS OF ARYL- AND ALKYL-SULFONYLDIAZOMETHANES

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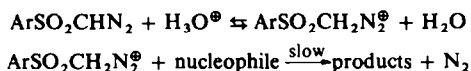
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Abstract—The mechanism of the acid-catalysed hydrolysis of aryl-, and in particular, alkylsulfonyldiazomethanes has been studied in water, 40% (v/v) dioxan-water and 60% (v/v) dioxan-water as the solvents. The reaction is specifically catalysed by hydronium ions as indicated by the solvent deuterium isotope effect. Strong evidence is presented for carbon protonation as the first step during the hydrolysis. Very fast H-D exchange of the methine proton was observed by PMR spectroscopy in 60% (v/v) dioxan-deuterium oxide solutions of strong acids and bases. In neutral 60% (v/v) dioxan-deuterium oxide solutions the rate constants of exchange could be evaluated. The logarithm of the pseudo first order rate constants of hydrolysis are linear in H_0 for $HClO_4$, HCl and H_2SO_4 as the catalysts. The slopes of these linear plots increase with increasing nucleophilicity of the conjugate base of the acid. At constant ionic strength the pseudo first order rate constants are linear in the acid concentration. At a constant $HClO_4$ concentration, the salts $NaClO_4$, $NaCl$ and $NaBr$ showed a positive salt effect which increased with increasing nucleophilicity of the anion. In acidic media containing chloride anions, the rate enhancement as compared with solutions containing the same amount of perchlorate anions, is directly correlated to the percentage of RSO_2CH_2Cl formed. A bimolecular rate determining step adequately accounts for the kinetic data. The activation parameter ΔS^\ddagger is also in the region of an A-2 mechanism. The nucleophilic contribution to the transition state is rather small. The oxibase scale has been used to correlate the nucleophilic sensitiveness of several diazonium ions.

INTRODUCTION

In a previous publication¹ we proposed a mechanism for the acid-catalysed hydrolysis of arylsulfonyldiazomethanes.² This mechanism was classified as the A-2 type of specific hydronium ion catalysis:



The occurrence of specific hydronium ion catalysis was the result of the electronic influence of the sulfonyl group on the diazo part of the molecule.¹

The present paper³ describes a kinetic study of the acid-catalysed hydrolysis of two alkylsulfonyldiazomethanes RSO_2CHN_2 (I, $R = PhCH_2$; II, $R = (Me_3C)$). Several arguments not used previously have been applied to elucidate the mechanism of hydrolysis for α -diazosulfones in more detail. The kinetic measurements of I were performed in water, 40% (v/v) dioxan-water and 60% (v/v) dioxan-water, those of II in 40% (v/v) dioxan-water. In addition some measurements were carried out with arylsulfonyldiazomethanes¹ $ArSO_2CHN_2$ ($Ar = p\text{-MeOC}_6\text{H}_4$ and $Ar = p\text{-MeC}_6\text{H}_4$).

RESULTS AND DISCUSSION

The proton transfer. The hydrolysis of α -diazosulfones is strongly catalysed by acids such as HClO_4 , H_2SO_4 and HCl and the reaction is definitely ionic in character.¹ Acid concentrations between 0.025 and 2.6N were necessary in order to obtain convenient reaction rates. The hydrolysis of I and II is specifically catalysed by hydronium ions on basis of the solvent deuterium isotope effect,⁴ k_D/k_H which is appreciably larger than unity (Table 1). A rapid equilibrium prior to a rate determining step is supported by the observation of fast hydrogen-deuterium exchange at the diazo carbon atom in acidic solutions by PMR spectroscopy.*

TABLE 1. THE SOLVENT DEUTERIUM ISOTOPE EFFECT AT 25°

Compound	Solvent	Acid concentration	% D ₂ O	k_D/k_H
I	water	0.0478N HClO_4	99.8	3.7
I	water	0.100N HClO_4	99.6	3.5
I	water	0.250N HClO_4	98.7	3.7
I	water	0.250N HClO_4 + 0.391 NaCl	98.7	4.7
I	water	0.493N HClO_4	97.4	5.3
I	water	0.847N HClO_4	96.0	4.8
I	water	0.225N HCl	98.3	4.4
I	water	0.319N HCl	97.7	5.1
I	water	0.541N HCl	96.5	4.7
I	water	0.996N H_2SO_4	99.1	5.0
I	water	1.517N H_2SO_4	98.6	4.3
I	40% dioxan-water	0.221N HClO_4	98.1	3.3
II	40% dioxan-water	1.409N HClO_4	88.5	2.3

TABLE 2. HYDROLYSIS OF *p*-METHOXYPHENYLSULFONYLDIAZOMETHANE IN AQUEOUS BUFFERS AT 40.00°

$C_{\text{ClCH}_2\text{COOH}}$ in mole/l	$C_{\text{ClCH}_2\text{COONa}}$ in mole/l	C_{NaClO_4} in mole/l	pH	$k_p \times 10^5$ sec ⁻¹
0.200	0.100		1.78	29.0
0.100	0.050	0.050	1.79	26.9
0.050	0.025	0.075	1.78	26.4

A well established test for specific hydronium ion catalysis is the measurement of the reaction rate in a series of buffers of different total concentration but with a constant ratio of acid to conjugate base. The results of the measurements with *p*-methoxyphenylsulfonyldiazomethane in chloroacetic acid-chloroacetate buffers, which are presented in Table 2, show that within the limits of accuracy the reaction rate only depends on the hydronium ion concentration.

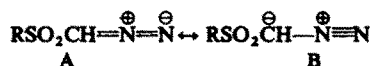
Formally three basic centra are present in the α -diazosulfones: the diazo carbon atom, the terminal N atom and the O atoms of the sulfonyl group. However, as will

*The exchange experiment for I has been carried out as described for *p*-methoxyphenylsulfonyldiazomethane and *t*-butylsulfonyldiazomethane.¹

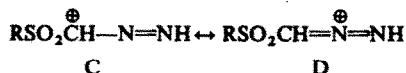
be argued below, we assume that the substrate *protonated at the diazo carbon atom* is the actual species involved in the rate determining liberation of N_2 .

The intermediacy of a species protonated at the sulfonyl oxygen can be excluded when the basicity of the sulfonyl group is considered in connection with the observed reaction rates. From the positions of the symmetric and asymmetric IR sulfone absorptions² it appears⁵ that I is considerable less basic than dimethylsulfone which* has a pK_b of +12.3. Using the data presented in Table 8 the rate constant of the slow step with chloride ions or water as nucleophile amounts to about 10^{10} – 10^{11} l.mole⁻¹ sec⁻¹, i.e. almost diffusion controlled. This rules out protonation of the sulfonyl group.

There are several arguments that favour C protonation over N protonation as the first step of the hydrolysis reaction. First of all, the conversion of RSO_2CHN_2 into $RSO_2CH_2N_2^{\oplus}$ will remove the resonance stabilization of the diazo part of the molecule and the system is prepared for the liberation of the very stable N_2 molecule. Secondly, the basicity of the terminal N atom will be decreased compared to alkyl-diazomethanes because of a larger contribution of resonance structure B (as indicated by spectral evidence²) due to the electron attracting effect of the sulfonyl group.



Furthermore, direct conjugation of the positive charge in C and D with the sulfonyl group is highly unfavourable.



The deshielding effect observed for the $-CHN_2$ signal in the PMR spectrum of *p*-methoxyphenylsulfonyldiazomethane, benzylsulfonyldiazomethane and *t*-butylsulfonyldiazomethane with increasing concentration in deuteriochloroform shows that intermolecular hydrogen bonding actually exists in the unprotonated α -diazosulfones (Table 3). Hydrogen bonding will be even more pronounced for the polar and highly acidic diazonium ion and will enhance⁶ the rate of exchange of the methine protons of the diazo moiety *via* protonation of the diazo carbon atom. In

TABLE 3. CONCENTRATION DEPENDENCE OF THE CHEMICAL SHIFT OF THE METHINE PROTON IN *p*-MeOC₆H₄SO₂CHN₂, PhCH₂SO₂CHN₂ AND Me₃CSO₂CHN₂ (SOLUTIONS IN CDCl₃, TMS AS INTERNAL STANDARD)

<i>p</i> -MeOC ₆ H ₄ SO ₂ CHN ₂		PhCH ₂ SO ₂ CHN ₂		Me ₃ CSO ₂ CHN ₂	
Concentration by wt %	δ (ppm)	Concentration by wt %	δ (ppm)	Concentration by wt %	δ (ppm)
6.4	5.27	4.7	4.99	4.6	5.03
14.6*	5.31	11.0	5.04	13.0	5.11
30.0	5.37			23.3	5.17

* δ in CD₃OD 5.94 ppm, indicating intramolecular hydrogen bonding.

* pK_a values have been calculated relative to the H₀ function of 100% H₂SO₄. Some uncertainty is included in their absolute values.

fact, the protonation of the diazo carbon atom may resemble the mechanism proposed by Corey and Lowry⁷ for the protonation of α -sulfonyl carbanions.

TABLE 4. RATES OF HYDROGEN-DEUTERIUM EXCHANGE FOR α -DIAZOSULFONES IN 60% DIOXAN-DEUTERIUM OXIDE

Compound	Catalyst	Temp (°C)	$k_{ex} \times 10^5$ (sec ⁻¹)	$k_p \times 10^{5a}$ (sec ⁻¹)
PhCH ₂ SO ₂ CHN ₂		37.7 ± 0.8	36	19.9
PhCH ₂ SO ₂ CHN ₂	0.400N NaClO ₄	37.7 ± 0.8	158	
PhCH ₂ SO ₂ CHN ₂	0.400N NaCl	37.7 ± 0.8	68	
Me ₃ CSO ₂ CHN ₂		37.7 ± 0.8	34	c. 0.91†
<i>p</i> -MeOC ₆ H ₄ SO ₂ CHN ₂		37.7 ± 0.8	96	109
<i>p</i> -MeOC ₆ H ₄ SO ₂ CHN ₂		25.5 ± 0.5	20	
<i>p</i> -MeC ₆ H ₄ SO ₂ CHN ₂		37.7 ± 0.8	42	47.0
<i>p</i> -MeC ₆ H ₄ SO ₂ CHN ₂	0.100 N NaClO ₄	37.7 ± 0.8	99	
<i>p</i> -MeC ₆ H ₄ SO ₂ CHN ₂	0.400 N NaClO ₄	37.7 ± 0.8	140	
<i>p</i> -MeC ₆ H ₄ SO ₂ CHN ₂	0.100 N NaCl	37.7 ± 0.8	53	
<i>p</i> -MeC ₆ H ₄ SO ₂ CHN ₂	0.400 N NaCl	37.7 ± 0.8	89	
<i>p</i> -MeC ₆ H ₄ SO ₂ CHN ₂	0.061 N CH ₃ COOH	37.7 ± 0.8	95	
<i>p</i> -MeC ₆ H ₄ SO ₂ CHN ₂	0.014 N HClO ₄	37.7 ± 0.8	very fast ‡	
<i>p</i> -MeC ₆ H ₄ SO ₂ CHN ₂	0.013 N K ₂ CO ₃	37.7 ± 0.8	very fast	

* Value of k_p in 0.400N HClO₄ in 40% dioxan-water at 25°, see Ref. 1.

† By extrapolation of the relation $\log k_p$ vs. $-\text{H}_0$.

‡ Rate of hydrolysis under the same conditions $k_p < 10^{-5}$ sec⁻¹.

It was possible to estimate the rate of deuteration in 60% dioxan—deuterium oxide* mixtures from the rate of exchange of RSO₂CHN₂ to RSO₂CDN₂ (Table 4). The larger rate of exchange of *p*-MeOC₆H₄SO₂CHN₂ as compared to *p*-MeC₆H₄SO₂CHN₂ suggests that the mechanism of exchange involves a rate-controlling protonation to give the diazonium ion which is then rapidly deprotonated by a solvent molecule. Since exchange is much more rapid than hydrolysis, N₂ is expelled only very rarely during the process of exchange. A simple steady state treatment ($c_{D_2O} \gg c_{RSO_2CHN_2}$) shows that the pseudo first-order rate constant of exchange (k_{ex}) is proportional to the rate constant of deuteration (k_d): $k_{ex} = e \cdot k_d$. In this equation the constant e determines the solvent deuterium isotope effect on this reaction. In diluted strong acids the exchange is very fast. In neutral 60% dioxan—deuterium oxide solutions sodium perchlorate exhibits a larger positive salt effect on the exchange of I than sodium chloride. It is noteworthy that the ratio of k_{ex} values for *p*-MeOC₆H₄SO₂CHN₂ and *p*-MeC₆H₄SO₂CHN₂ is about the same as the ratio of the respective k_p values for hydrolysis in 0.4N HClO₄ in 40% dioxan-water¹. The rate of deuteration of I and II is larger than anticipated from comparison of their k_p values with those of the arylsulfonyldiazomethanes. The k_{ex} values at 25.5° and 37.7° for *p*-MeC₆H₄SO₂CHN₂ permit a rough estimation of the ΔS^\ddagger value for the exchange reaction. The calculated slightly positive value (about 4 e.u.) is within the expected range for this type of reaction.⁸

* The deuterium oxide had p^D 6.8. The salts used in the exchange measurements contained no acid.

The fast exchange reaction in alkaline media* (Table 4) may proceed *via* the carbanion $\text{RSO}_2\overset{\ominus}{\text{C}}\text{N}_2$ on the analogy of the ion $\text{RCO}\overset{\ominus}{\text{C}}\text{N}_2$ proposed by Morrison and Yates⁹ for the base-catalysed hydrogen to deuterium exchange in α -diazoketones.

In 60% dioxan-deuterium oxide mixtures the rate of exchange in α -diazacetophenone is very slow compared with that of the α -diazosulfones. After 8 days at about 20° only 60% exchange had occurred (in this time interval decomposition of the α -diazoketone was negligible). In *acidic media* this picture is maintained³ as appeared from the work of Dahn and Gold.¹⁰ This slower exchange rate is in line with the behaviour of α -sulfonyl- and α -carbonyl carbanions, the former being protonated more rapidly than the latter.¹¹

Rate dependence on the acidity of the medium. The two alkylsulfonyldiazomethanes I and II showed a linear relationship between $\log k_p$ and Hammett's acidity function¹²⁻¹⁴ H_0 for HClO_4 , H_2SO_4 and HCl as catalyst in water or in 40% and 60% dioxan-water solutions. (Fig. 1 and Table 5).

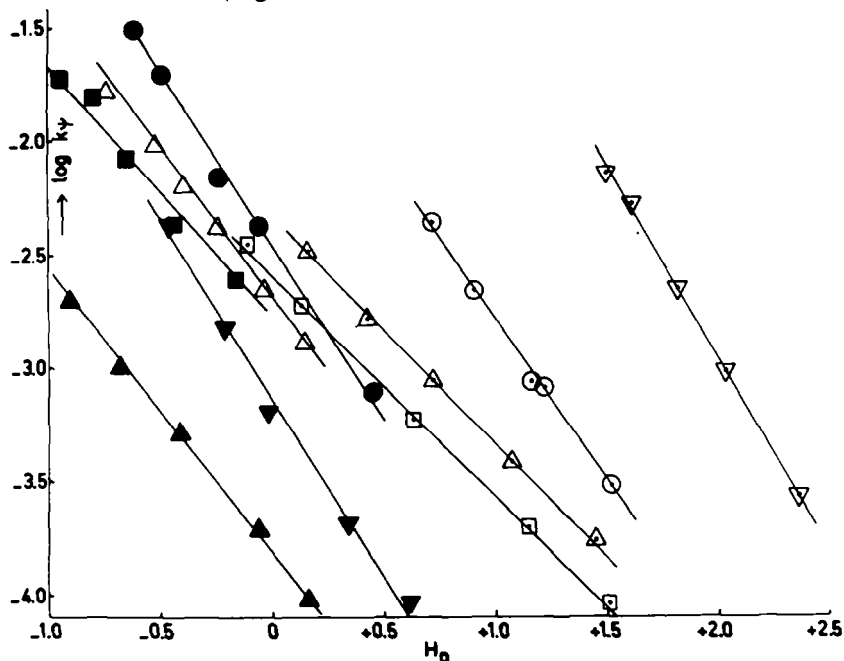


FIG. 1. Relation between $\log k_p$ and H_0 in the hydrolysis of benzylsulfonyldiazomethane (I) and *t*-butylsulfonyldiazomethane (II) at 25°

- I in H_2O ; HClO_4
- I in H_2O ; HCl
- △ I in H_2O ; H_2SO_4
- I in 40% dioxan- H_2O ; HClO_4
- I in 40% dioxan- H_2O ; HCl
- △ I in 60% dioxan- H_2O ; HClO_4
- ▽ I in 60% dioxan- H_2O ; HCl
- ▲ II in 40% dioxan- H_2O ; HClO_4
- ▼ II in 40% dioxan- H_2O ; HCl

* In the presence of sodium hydroxide decomposition occurs with formation of red coloured products.

TABLE 5. THE ACID-CATALYSED HYDROLYSIS OF I AND II AT 25°

Compound	Solvent	Catalyst	Slope of $\log k_{\psi}$ vs. $-H_0$	Slope of $k_{\psi}^{\text{HCl}}/k_{\psi}^{\text{HClO}_4}$ (H_0) vs. c_{Cl^-}
I	H ₂ O	HClO ₄	1.17	
I	H ₂ O	H ₂ SO ₄	1.28	
I	H ₂ O	HCl	1.55	2.0
I	40% dioxan-H ₂ O	HClO ₄	0.95	
I	40% dioxan-H ₂ O	HCl	1.46	7.6
I	60% dioxan-H ₂ O	HClO ₄	0.98	
I	60% dioxan-H ₂ O	HCl	1.7	c. 50
II	40% dioxan-H ₂ O	HClO ₄	1.13	
II	40% dioxan-H ₂ O	HCl	1.56	c. 3.0

The slopes of $\log k_{\psi}$ vs. $-H_0$ are usually larger than unity and increased with increasing nucleophilic character of the conjugate base of the catalyst ($\text{HClO}_4 < \text{H}_2\text{SO}_4 < \text{HCl}$). Using the Zucker-Hammett criterion, the slope of about unity would imply that an A-1 mechanism operates.¹⁵ However, this empirical criterion is only useful in the case of N and O bases and is especially unreliable for hydrocarbon-like bases as has been argued before.¹ The only fairly safe conclusion that can be drawn from the relation $\text{dlog } k_{\psi} = -c \cdot \text{d}H_0$ (c is a constant) for HClO_4 is, that the transition state of the slow step has approximately the same amount of hydrogen bonding as the protonated Hammett indicators. Plots of $\log k_{\psi}$ vs. $-H'_R$ (Ref. 16) show a straight line, however with a slope appreciably less than unity (about 0.5), suggesting no similarity in the solvation of the transition state of the slow step and the protonated olefins by means of which the H'_R function has been defined. Schubert and Quacchia¹⁷ have clearly demonstrated that with increasing importance of hydrogen bonding carbon bases tend to follow $-H_0$ rather than $-H'_R$.

The greater slope of $\log k_{\psi}$ vs. $-H_0$ for HCl than for HClO_4 and the faster reaction in HCl solution as compared with HClO_4 at the same H_0 indicate that a nucleophile participates in the transition state of the slow step. The rate enhancement by chloride ions is demonstrated by the plots of $k_{\psi}^{\text{HCl}}/k_{\psi}^{\text{HClO}_4}$ (at the same H_0) against the chloride ion concentration which show straight lines with positive slopes (Fig. 2 and Table 5).

For benzyldiazomethane I in aqueous HClO_4 the Bunnett-criterion¹⁸ can be applied. Despite some scattering of the points, a w -value of about -4 has been evaluated from a plot of $\log k_{\psi} + H_0$ vs. $\log a_{\text{H}_2\text{O}}$. For hydrocarbon-like bases Bunnett¹⁸ suggested a w -value of about -3 in the case of an A-2 mechanism. Unfortunately, the lack of well defined examples makes this empirical criterion questionable.

If the ionic strength μ is kept constant by the addition of the sodium salt of the acid catalyst and the acid-salt ratio is varied, the rates of hydrolysis of I in aqueous solution are proportional to the acid concentration (Fig. 3): $\text{d}k_{\psi} = c' \cdot \text{d}c_{\text{H}^+}$. This relationship was observed for HClO_4 - NaClO_4 ($\mu = 1.596$ resp. 2.543M) and HCl - NaCl ($\mu = 1.596\text{M}$) solutions. The constant c' depends clearly on the ionic strength

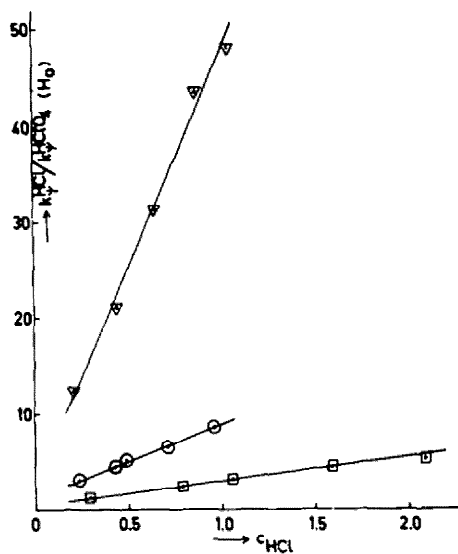


FIG. 2. Plot of $k_p^{\text{HCl}}/k_p^{\text{HClO}_4} (H_0)$ vs. c_{HCl} (mole/l) for the hydrolysis of benzylsulfonyldiazomethane at 25°

- H₂O
- 40% dioxan-H₂O
- ▽ 60% dioxan-H₂O

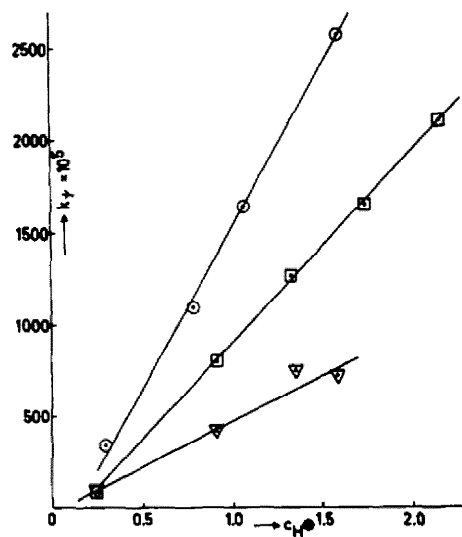


FIG. 3. Relation between k_p (sec⁻¹) and c_{H}^0 (mole/l) for the hydrolysis of benzylsulfonyldiazomethane at constant ionic strength

- HCl + NaCl; $\mu = 1.596$
- HClO₄ + NaClO₄; $\mu = 2.543$
- ▽ HClO₄ + NaClO₄; $\mu = 1.596$

and on the nature of the catalyst. The linear relationship demonstrates that the effect of the activity coefficients is constant in media of constant ionic strength. In these HCl-NaCl solutions $75 \pm 2\%$ benzyl chloromethyl sulfone is formed, independent of the HCl-NaCl ratio. Thus, the nature of the cation does not influence the product determining slow step. Both an A-1 or an A-2 mechanism can account for these observations.

Salt effects. The effect of NaClO₄, NaCl and NaBr on the reaction rate of I in aqueous solution at a constant acid concentration (0.253N HClO₄) was determined at 25°. As in the case of arylsulfonyldiazomethanes, the salt with the most nucleophilic anion showed the largest acceleration of the reaction rate. As shown in Fig. 4 the effect of perchlorate anions on k_{ψ} is linear in the salt concentration, whereas the effect of halide anions is non-linear.

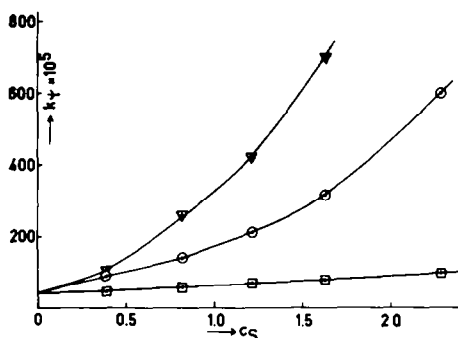


FIG. 4. Plot of k_{ψ} (sec^{-1}) vs. the salt concentration c_s (mole/l) for the hydrolysis of benzylsulfonyldiazomethane in 0.253N HClO₄ at 25°

- NaClO₄
- NaCl
- ▽ NaBr

The salt effects can only be reconciled with nucleophilic attack by halide on the diazonium ion.

Semiquantitative treatment of the rate enhancement by chloride anions. If the hydrolysis of α -diazosulfones would follow an A-1 pattern, subjected to only a specific medium induced salt effect of chloride anions, no correlation would be expected between the salt effect on the rate determining step and the salt effect on the subsequent fast product determining steps. However, assuming that the extra rate accelerating effect of chloride anions is due to nucleophilic attack on an intermediate, it is possible to correlate the product ratio $\text{RSO}_2\text{CH}_2\text{Cl}(\text{RSO}_2\text{H} + \text{CH}_2\text{O})$ and the increase in rate by chloride anions.

For an A-2 mechanism, the rate equation in HClO₄ solution reads (DA = α -diazosulfone):

$$-\frac{dc_{\text{DA}}}{dt} = k_{\psi}^{\text{HClO}_4} \cdot c_{\text{DA}} = k_{\text{H}} \cdot c_{\text{DA}} \cdot c_{\text{H}}^{\oplus} \cdot c_{\text{H}_2\text{O}} \quad (1)$$

TABLE 6. RATE ENHANCEMENT AND PRODUCT COMPOSITION FOR THE HYDROLYSIS OF I AND II AT 25°

Compound	Solvent	c_{HCl} (mole/l)	H_0	$k_{\text{HCl}}^{\text{H}} \times 10^5$ (sec^{-1})	$k_{\text{HClO}_4}^{\text{H}} \times 10^5$ (sec^{-1}) (same H_0)	Percentage of $\text{PhCH}_2\text{SO}_2\text{CH}_2\text{Cl}$ Found	Percentage of $\text{PhCH}_2\text{SO}_2\text{CH}_2\text{Cl}$ Calc
I	H ₂ O	0.297	+0.47	74.0	52.0	37	30
I	H ₂ O	0.791	-0.06	439	178	66	59
I	H ₂ O	1.067	-0.24	857	282	74	67
I	H ₂ O	1.596	-0.51	2590	585	80	77
I	H ₂ O	2.086	-0.72	4840	1020	85	80
I	40% dioxan-H ₂ O	0.240	1.52	29.2	9.30	78	68
I	40% dioxan-H ₂ O	0.433	1.23	77.0	17.4	83	77
I	40% dioxan-H ₂ O	0.496	1.15	108	19.9	88	82
I	40% dioxan-H ₂ O	0.710	0.91	211	34.7	90	85
I	40% dioxan-H ₂ O	0.965	0.72	441	52.5	92	88
I	60% dioxan-H ₂ O	0.217	2.35	27.9	c. 2.2		
I	60% dioxan-H ₂ O	0.435	2.03	95.5	c. 4.7	93	95
I	60% dioxan-H ₂ O	0.649	1.82	237	c. 7.6		
I	60% dioxan-H ₂ O	0.878	1.62	532	c. 10.0		
I	60% dioxan-H ₂ O	1.049	1.49	750	c. 16.0	100	98
II	40% dioxan-H ₂ O	1.091	0.62	9.27	2.50		
II	40% dioxan-H ₂ O	1.518	0.33	21.6	7.25		
II	40% dioxan-H ₂ O	2.145	0.01	63.7	17.4		
II	40% dioxan-H ₂ O	2.656	-0.22	156	30.2		
II	40% dioxan-H ₂ O	3.130	-0.47	430	57.6		

and in HCl solution:

$$\frac{-dc_{DA}}{dt} = k_{\psi}^{HCl} \cdot c_{DA} = k_H \cdot c_{DA} \cdot c_{H^{\oplus}} \cdot c_{H_2O} + k_{Cl} \cdot c_{DA} \cdot c_{H^{\oplus}} \cdot c_{Cl^{\ominus}} \quad (2)$$

In these equations k_H and k_{Cl} are dependent on the acid concentration because they contain the respective activity coefficients. The term $k_H \cdot c_{DA} \cdot c_{H^{\oplus}} \cdot c_{H_2O}$ measures the amount of RSO_2CH_2OH (dissociated into RSO_2H and CH_2O) formed at a particular HCl concentration and the term $k_{Cl} \cdot c_{DA} \cdot c_{H^{\oplus}} \cdot c_{Cl^{\ominus}}$ the amount of RSO_2CH_2Cl . In the following discussion the reasonable but basic assumption* will be made that the substrate is protonated to the same extent at the same H_0 values in $HClO_4$ and HCl solutions of moderate acidity. This allows the substitution of Eqn (1) in Eqn (2) and the term $k_{Cl} \cdot c_{DA} \cdot c_{H^{\oplus}} \cdot c_{Cl^{\ominus}}$ can be evaluated at a particular H_0 .

For benzyldiazomethane (I) the product ratio has been determined in aqueous HCl, in aqueous $HClO_4$ with added NaCl and in HCl solutions in 40% and 60% dioxan-water. Tables 6 and 7 show that, within experimental error, the rate enhancement by chloride ions correlates satisfactorily with the amount of $PhCH_2SO_2CH_2Cl$ formed during hydrolysis. Therefore the reaction with chloride ions follows the A-2 pattern.† In addition, the observed correlation suggests that the reaction with water has also a nucleophilic contribution to the transition state of the slow step, because in the case of an A-1 process with water in the presence of chloride ions, additional quantities of $PhCH_2SO_2CH_2Cl$ would be formed from the carbonium ion.

TABLE 7. SALT EFFECT OF $NaClO_4$, NaCl AND NaBr ON THE RATE OF HYDROLYSIS OF I IN 0.253N $HClO_4$ AT 25°

c_{sub} (mole/l)	$k_{\psi}^{NaClO_4} \times 10^5$ (sec ⁻¹)	$k_{\psi}^{NaCl} \times 10^5$ (sec ⁻¹)	Percentage of $PhCH_2SO_2CH_2Cl$ Found	Percentage of $PhCH_2SO_2CH_2Cl$ Calc	$k_{\psi}^{NaBr} \times 10^5$ (sec ⁻¹)
0.391	47.3	82.6	33	43	101
0.818	58.8	142	55	59	259
1.210	70.2	209	67	67	419
1.627	82.0	316	74	74	700
2.290	96.9	598	80	83	

Starting from the *observed* fractions F of benzyl chloromethyl sulfone formed, the rate constants k_H and k_{Cl} at a particular acid concentration can be evaluated by means of the equations:

$$k_{Cl} \cdot c_{H^{\oplus}} \cdot c_{Cl^{\ominus}} = k_{\psi}^{HCl} \cdot F \quad (3)$$

$$k_H \cdot c_{H^{\oplus}} \cdot c_{H_2O} = k_{\psi}^{HCl} \cdot (1-F) \quad (4)$$

The values of $k_H \cdot c_{H_2O}$ and k_{Cl} for the hydrolysis of I in aqueous HCl and in 0.253N $HClO_4$ with added NaCl are collected in table 8.

* Deviations will only be found for weak non-Hammett bases in very concentrated acidic media.

† W. J. Albery and R. P. Bell (*Trans. Faraday Soc.* 57, 1942 (1961)) have proposed an A-2 mechanism for the hydrolysis of ethyl diazoacetate using essentially the same argument, although they did not always carry out product analyses and kinetic measurements in the same solution. Adopting the method depicted by us to the results of these authors gives within experimental error the same agreement between rate acceleration and chloroacetic ester formation.

TABLE 8. RATE CONSTANTS FOR THE REACTION OF I WITH WATER (k_H) AND CHLORIDE ION (k_{Cl})

c_{HCl}	c_{HClO_4}	c_{NaCl}	Fraction of $PhCH_2SO_2CH_2Cl$ Found	$k_H \cdot c_{H_2O} \times 10^5$ ($l \text{mole}^{-1} \text{sec}^{-1}$)	$k_{Cl} \times 10^5$ ($l^2 \text{mole}^{-2} \text{sec}^{-1}$)
0.297			0.37	157	311
0.791			0.66	188	464
1.067			0.74	209	557
1.596			0.80	326	808
2.086			0.85	350	944
	0.253	0.391	0.33	221	280
	0.253	0.818	0.55	256	381
	0.253	1.210	0.67	276	463
	0.253	1.627	0.74	328	574
	0.253	2.290	0.80	480	835

TABLE 9. RATE CONSTANTS EXTRAPOLATED TO ZERO IONIC STRENGTH

Compound	Solvent	Catalyst	$k_H^0 \times 10^5$ ($l^2 \text{mole}^{-2} \text{sec}^{-1}$)	$k_{Cl}^0 \times 10^5$ ($l^2 \text{mole}^{-2} \text{sec}^{-1}$)
$PhCH_2SO_2CHN_2$	H_2O	$HClO_4$	2.6	
$PhCH_2SO_2CHN_2$	H_2O	HCl	2.6	155
$PhCH_2SO_2CHN_2$	H_2O	0.253N $HClO_4$ + $NaCl$	2.6	140
$PhCH_2SO_2CHN_2$	40% dioxan- H_2O	HCl	0.93	c. 340
$PhCH_2SO_2CHN_2$	60% dioxan- H_2O	HCl	0.72	c. 500
$Me_3CSO_2CHN_2$	40% dioxan- H_2O	HCl	0.036	c. 4.0
$p\text{-NO}_2C_6H_4SO_2CHN_2$	H_2O	HCl	0.71	c. 89

* Calculated with $c_{H_2O} = 55M$.

Estimates of k_H^0 ($= k_H$ at ionic strength $\mu = 0$) could be made by extrapolation to zero ionic strength by the use of the equation, $\ln k_H = \ln k_H^0 + B\mu$, originally derived for the reaction between an ion (in this case the diazonium ion) and a neutral dipolar molecule (water) in dilute solutions.^{19,20} Although the reaction media employed are outside the range of diluted solutions, excellent straight lines were obtained by plotting $\log(k_H^{HClO_4}/c_{H^{\oplus}}) = \log(k_H \cdot c_{H_2O})$ vs. μ for $HClO_4$ solutions in water, in 40% and 60% dioxan-water (Table 9). The same treatment was applied to the $k_H \cdot c_{H_2O}$ values (Table 8) obtained from Eqn (4), which gave k_H^0 values in excellent agreement (Table 9) with that found in $HClO_4$ solution (in the latter case $k_H^0 \cdot c_{H_2O}$ was obtained by extrapolating $\log(k_H^{HClO_4}/c_{H^{\oplus}})$ to $\mu = 0$).

In solutions containing chloride ions, $\log k_{Cl}$ is proportional to $\sqrt{\mu}$ as has been predicted¹⁹ for a reaction between two oppositely charged ions.³ In aqueous HCl (k_{Cl} values from Table 8) k_{Cl}^0 ($= k_{Cl}$ at $\mu = 0$) was found by extrapolating $\log k_{Cl}$ to $\sqrt{\mu} = 0$ (Table 9). In the case of 0.253N $HClO_4$ with added $NaCl$ (k_{Cl} values from Table 8) extrapolation of $\log k_{Cl}$ to $\sqrt{c_{NaCl}} = 0$ gave k_{Cl}^0 (Table 9). Reasonable agreement exists between the k_{Cl}^0 values evaluated for both cases.

Since less extensive data on the product composition are available for the hydrolysis of I and II in solutions of HCl in 40% or 60% dioxan-water, the k_{Cl} values at a particular HCl concentration were determined by means of the Eqns (1) and (2) and assuming the same steady-state concentration of the diazonium ion at the same H_0 in HClO_4 and HCl. By plotting $\log k_{\text{Cl}}$ vs. $\sqrt{\mu}$ and extrapolating to $\sqrt{\mu} = 0$, the k_{Cl}^0 values (Table 9) were found.

For I in aqueous HCl the ratio $k_{\text{Cl}}^0/k_{\text{H}}^0$ amounts to about 56 and shows that the reaction is rather insensitive to nucleophilic attack, just as was proposed for the arylsulfonyldiazomethanes.¹ The value of k_{Cl}^0 increases with decreasing polarity of the medium as expected for a bimolecular reaction between two ions.¹⁹

The evaluation of k_{H}^0 and k_{Cl}^0 (Table 9) for the hydrolysis of *p*-nitrophenylsulfonyldiazomethane in aqueous HCl was carried out in the same way as described for I using the data published previously.¹

The reaction rates of substrates with various nucleophiles relative to water at 25° have been successfully correlated by Edwards²¹ in a four parameter equation. Recently Davies^{22,23} extended this theory and renamed it the oxibase scale:

$$\log \frac{k_{(\text{X})}}{k_{(\text{H}_2\text{O})}} = \alpha E + \beta H \quad (\text{X} = \text{nucleophile})$$

In this equation $k_{(\text{X})}/k_{(\text{H}_2\text{O})}$ is the relative rate of X compared to water, E and H are characteristic constants for the nucleophile and α and β are constants for the substrate.

In Table 10 values for $k_{(\text{X})}/k_{(\text{H}_2\text{O})}$ are shown for $\text{MeCOCH}_2\text{N}_2^\oplus$ (as calculated with the oxibase scale parameters²²) together with the approximate values for $\text{PhCH}_2\text{SO}_2\text{CH}_2\text{N}_2^\oplus$ and *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{N}_2^\oplus$ derived from our kinetic results

TABLE 10. SENSITIVITY TO NUCLEOPHILIC ATTACK OF SOME DIAZONIUM IONS IN AQUEOUS SOLUTIONS AT 25°

Diazonium ion	Nucleophile X	E	H	α	β	$\frac{k_{(\text{X})}}{k_{(\text{H}_2\text{O})}}$
$\text{MeCOCH}_2\text{N}_2^\oplus$	Cl^\ominus	1.24	-3	2.37	0.191	230
$\text{MeCOCH}_2\text{N}_2^\oplus$	Br^\ominus	1.51	-6	2.37	0.191	270
$\text{MeCOCH}_2\text{N}_2^\oplus$	ClO_4^\ominus	-0.73	-9	2.37	0.191	3.5×10^{-4}
$\text{EtOOCCH}_2\text{N}_2^\oplus$	Cl^\ominus	1.24	-3			150
$\text{PhCH}_2\text{SO}_2\text{CH}_2\text{N}_2^\oplus$	Cl^\ominus	1.24	-3	c. 1.7	c. 0.12	56
$\text{PhCH}_2\text{SO}_2\text{CH}_2\text{N}_2^\oplus$	Br^\ominus	1.51	-6	c. 1.7	c. 0.12	c. 72*
$\text{PhCH}_2\text{SO}_2\text{CH}_2\text{N}_2^\oplus$	ClO_4^\ominus	-0.73	-9	c. 1.7	c. 0.12	c. 5×10^{-3}
<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{N}_2^\oplus$	Cl^\ominus	1.24	-3			c. 125

* Approximate value obtained from the salt effect of NaBr in aqueous 0.253N HClO_4 .

(k_{Cl}^0 and k_{H}^0) and the value for $\text{EtO}_2\text{CCH}_2\text{N}_2^\oplus$ calculated from the data given by Albery and Bell.* An estimate of the α and β values for the decomposition of the benzylsulfonylmethyldiazonium ion has been made (Table 10).

The acid-catalysed hydrolysis of α -diazosulfones has clearly less nucleophilic assistance than that of ethyl diazoacetate* and diazoacetone.²⁴ The difference

* See footnote † on p. 1746.

TABLE 11. ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF BENZYL-SULFONYLDIAZOMETHANE AND *t*-BUTYLSULFONYLDIAZOMETHANE

Compound	Solvent	Catalyst	$k_p \times 10^5$ (sec ⁻¹) 25°	$k_p \times 10^5$ (sec ⁻¹) 40°	ΔH^\ddagger (kcal/mole)	ΔS^\ddagger (e.u.)
PhCH ₂ SO ₂ CHN ₂	H ₂ O	0.253N HClO ₄ *	42.6	172	17.4	-16
PhCH ₂ SO ₂ CHN ₂	H ₂ O	1.069N HClO ₄	282	1260	17.9	-10
PhCH ₂ SO ₂ CHN ₂	H ₂ O	1.076N HCl	870	3800	17.6	-9
PhCH ₂ SO ₂ CHN ₂	40% dioxan-H ₂ O	0.220N HClO ₄	9.34	42.1	18.0	-16
PhCH ₂ SO ₂ CHN ₂	40% dioxan-H ₂ O	1.206N HClO ₄	169	644	16.0	-17
PhCH ₂ SO ₂ CHN ₂	40% dioxan-H ₂ O	0.240N HCl	29.2	123	17.2	-17
PhCH ₂ SO ₂ CHN ₂	60% dioxan-H ₂ O	0.481N HClO ₄	18.3	82.6	18.0	-15
PhCH ₂ SO ₂ CHN ₂	60% dioxan-H ₂ O	0.230N HCl	31.8	131	16.9	-18
Me ₃ CSO ₂ CHN ₂	40% dioxan-H ₂ O	1.645N HClO ₄	19.8	106	20.1	-8
Me ₃ CSO ₂ CHN ₂	40% dioxan-H ₂ O	1.519N HCl	21.6	102	18.6	-13

* The ΔS^\ddagger and ΔH^\ddagger values were derived from a plot of $\log k_p$ vs. $1/T$, see Fig. 5.

between the α -diazosulfone and the α -diazoketone is primarily the result of a decrease in α . The β -value is slightly larger for $\text{MeCOCH}_2\text{N}_2^{\oplus}$ due to the greater electronegativity of the carbonyl group compared with the sulfonyl group.²⁵

Activation parameters. The activation parameters ΔH^\ddagger and ΔS^\ddagger for the hydrolysis reaction of the alkylsulfonyldiazomethanes in water (I), 40% dioxan-water (I and II) and 60% dioxan-water (I) are collected in Table 11.

Mechanistic evidence can be obtained especially from entropy values, but as Schalenger and Long⁸ have pointed out, the exact interpretation of entropy data for reactions in solutions is by no means straightforward. Nevertheless, the distinction between an A-1 and A-2 mechanism is at least in part possible by examination of ΔS^\ddagger data.²⁶ If *no* nucleophile is incorporated in the transition state of the slow step and only the C—N bond is somewhat longer than in the original diazonium ion, then there will be a decreased electrostatic interaction with the solvent due to the increased size of the ion. Thus, A-1 mechanisms will have positive ΔS^\ddagger values for the slow step. In the case of A-2 mechanisms, the bonding of a nucleophile in the transition state causes negative ΔS^\ddagger values. Using this criterion, the data in Table 11 are indicative for an A-2 process.

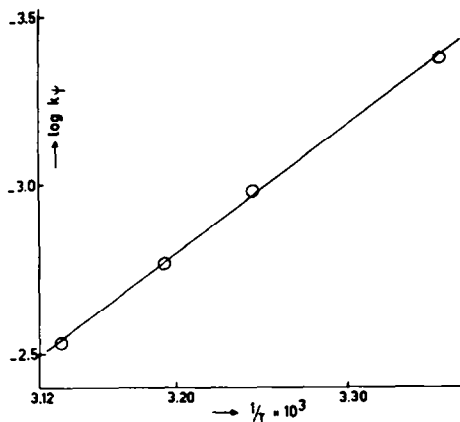


FIG. 5. Plot of $\log k_p$ vs. $1/T$ for the hydrolysis of benzylsulfonyldiazomethane in 0.253 N HClO_4 .

The ΔS^\ddagger value of the protonation is slightly positive when protonation occurs exclusively by the hydronium ion. This can be explained by the more effective solvation of the proton¹ compared with the diazonium ion. The activation parameters are the sum of those of the equilibrium step and the rate determining step. Consequently about 17 e.u. are lost in the transformation of the diazonium ion derived from I to the transition state for the loss of nitrogen. This is a reasonable value for the incorporation of a water molecule in a transition state without much bond making.^{8, *}

It should be noted that I gives an excellent straight line (Fig. 5) by plotting $\log k_p$ vs. $1/T$, which is in contrast to the somewhat puzzling results of Thomas and Leveson²⁷ for the hydrolysis of some α -diazoketones.

* Some entropy may be gained in the diazonium ion by extra possibilities for rotation compared to the more immobile $-\overset{\ominus}{\text{C}}\text{H}-\overset{\oplus}{\text{N}}\equiv\text{N}$ group.

Comparison of the activation parameters of I in 0.253N and 1.069N aqueous HClO_4 indicates that less hydrogen bonding occurs in the stronger acidic media because of a decrease in ΔS^\ddagger and a slight increase in ΔH^\ddagger . The less negative ΔS^\ddagger values and the higher ΔH^\ddagger values for II as compared with I may be the result of steric hindrance to solvation of the transition state of the slow step.

A rough comparison of the free enthalpy profiles³ for the acid-catalysed hydrolysis of 1-phenyl-3-diazoacetone¹⁰ and benzylsulfonyldiazomethane with the aid of the available kinetic data, reveals that the bimolecular second step for the α -diazosulfone requires about 4 kcal/mole more free enthalpy of activation than the slow step in the hydrolysis of the α -diazoketone.

Concluding remarks on the mechanism. On account of the evidence presented in the preceding sections, the mechanism that satisfactorily fits the available data is the A-2 type mechanism.

The small nucleophilic assistance in the decomposition of the sulfonylmethyldiazonium ions can chiefly be attributed to the good leaving ability of the very stable N_2 molecule, the steric²⁸ and field²⁹ effects of the sulfonyl group (especially in the case of negatively charged nucleophiles) and the initial position of the positive charge on the N atom instead of on the C atom on which the attack takes place. However, the field effect will be partially compensated by the electric influence of the positive charge on the diazonium ion.

Loosening of the C—N bond in the diazonium ion is accompanied by unfavourable accumulation of positive charge next to the electronegative sulfonyl group. Although the Hammond postulate³⁰ suggests that the transition state of the slow step will resemble the diazonium ion, it is reasonable to suppose that some delocalization of the positive charge in the α -position to the sulfonyl group by interaction with a nucleophile in the transition state will reduce the otherwise very high energy content of the system.

The mechanism of hydrolysis for alkyl- and arylsulfonyldiazomethanes is essentially the same. Before rationalizing minor changes in reactivity, it should be kept in mind that no large entropy differences between both types of α -diazosulfones are involved and that the rates of deuteration vary only little. Since it is reasonable to suppose¹¹ that $\text{PhCH}_2\text{SO}_2\text{CH}_2\text{N}_2^\oplus$ is more acidic than $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{N}_2^\oplus$, the slower rate of hydrolysis of benzylsulfonyldiazomethane (I) as compared with *p*-methylphenylsulfonyldiazomethane would be satisfactorily explained by assuming a lower steady-state concentration of $\text{PhCH}_2\text{SO}_2\text{CH}_2\text{N}_2^\oplus$. However, effects on the slow step have also to be considered because the ratio $k_{\text{Cl}^-}^0/k_{\text{H}_2\text{O}}^0$ for I and $p\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{CHN}_2$ shows that $\text{PhCH}_2\text{SO}_2\text{CH}_2\text{N}_2^\oplus$ is less discriminating towards nucleophiles than $p\text{-NO}_2\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{N}_2^\oplus$. (Table 10).

In order to picture an energy profile of the hydrolysis reaction, a pK_a value of about -3 for the sulfonylmethyldiazonium ions was estimated.* Using this value and the data from Table 11, a ΔG^\ddagger value of about 14 kcal/mole was calculated for the bimolecular step. This rather low energy requirement causes that small changes in solvation of the diazonium ion proceeding to the transition state of the slow step, can play an important role.

* The guess has been made by taking into account, (1) the rate of protonation of I; (2) the electron attracting power of the $-\overset{\oplus}{\text{N}}\equiv\text{N}$ moiety and the sulfonyl group; (3) the presence of a positive charge.

The variation of k_D/k_H with the acid concentration* (Table 1) may be the result of a somewhat decreased solvation³¹ of the transition state in the more acidic media (due to a decrease in a_{H_2O}). This results in a stronger bonding of a proton (or deuteron) to the diazo molecule and consequently will cause a larger loss of zero point energy of the proton under these conditions.

α -Diazoketones are less readily protonated but more easily hydrolysed¹ than the structurally corresponding α -diazosulfones. The slow step in the hydrolysis of the α -diazoketones has apparently lower energy requirements which is in line with the favourable influence of an α -carbonyl group on nucleophilic displacement reactions.³² This neighbouring group overlap effect explains the higher $k_{(X)}/k_{(H_2O)}$ values† for the α -diazoketones and again confirms the bimolecular character of the slow step in the hydrolysis of α -diazosulfones and α -diazoketones.

EXPERIMENTAL

Methods. Pseudo first-order rate constants of hydrolysis k_p were obtained by the kinetic procedure described in the previous paper.¹ In all cases the room temp was kept at $25.0 \pm 0.3^\circ$. For I the selected wavelength was 230 μ (water) or 380 μ (dioxan-water), for II 380 μ (dioxan-water). Rate constants were averaged over two or more measurements and were reproducible to within 3%.

Reactions at temps above 25° and those with half life times less than 8 min were carried out in adequately thermostated cell compartments (Zeiss PMQ II, 2 cm cells, equipped with a magnetic stirring device).

Estimates of the RSO_2CHN_2 - RSO_2CDN_2 exchange rate in 60% (v/v) dioxan- D_2O with or without added catalyst were made by means of a Varian A-60 PMR spectrometer. The solvent (or soln) (1.2 ml) was thermostated prior to use and the α -diazosulfone (about 45 mg) was then dissolved as quickly as possible. The soln was kept in the probe ($37.7 \pm 0.8^\circ$) during the whole reaction time (100% exchange). The integrated $-CHN_2$ signal I_t was measured as a function of time. By plotting $\log I_t$ against time, reasonably straight lines were obtained from which the pseudo first-order rate constants of exchange k_{ex} were evaluated. Some experiments were carried out at $25.5 \pm 0.5^\circ$ using the Varian variable temp probe. The temp inside the reaction mixture was measured with a thermocouple. The experimental error in k_{ex} was estimated to be roughly 20%, chiefly because of temp fluctuations. After complete exchange the presence of RSO_2CDN_2 was ensured by addition of water, which resulted in the reappearance of the $-CHN_2$ signal.

Materials, solvents, reagents. The α -diazosulfones were prepared by the method of Van Leusen and Strating.² The purification and preparation of the solvents and chemicals was reported previously.¹

Benzyl hydroxymethyl sulfone (III) was prepared by dissolving benzyldisulfonic acid³³ (0.013 mole) in 5 ml water and 1.5 ml of 36% formaldehyde in water. This mixture was kept at about 60° for 4 min and then cooled to 20° . White crystals separated which were collected and washed with 20 ml benzene (yield 95%, m.p. 110 – 115°).

Recrystallization from MeOH at low temp furnished 60% of the analytically pure III, m.p. 114 – 118° dec. (Found: C, 51.85; H, 5.50; S, 16.77. Calc. for $C_8H_{10}O_3S$: C, 51.60; H, 5.41; S, 17.22%.)

The PMR spectrum of a 10% soln in hexadeuteroacetone showed two peaks of equal intensity at τ 5.63 ppm and τ 5.55 ppm (methylene protons), one peak at about τ 2.60 ppm (aromatic protons) and a broadened signal (OH group) at about τ 5.0 ppm. The IR spectrum (KBr) exhibited absorptions at 3400 cm^{-1} (OH group), 1130 and near 1300 cm^{-1} (sulfonyl group).

Reaction products. Compound I decomposes very slowly in pure water at 25° . After 24 hr approximately 20% decomposition had taken place as indicated by the change in the UV spectrum.‡ After 56 days the

* A variation of the solvent deuterium isotope effect with the acid concentration has also been found (but not interpreted) for the generally acid catalysed decomposition of diphenyldiazomethane in toluene in the presence of benzoic acid: R. A. More O'Ferrall, W. K. Kwok and S. J. Miller, *J. Am. Chem. Soc.* **86**, 5553 (1964).

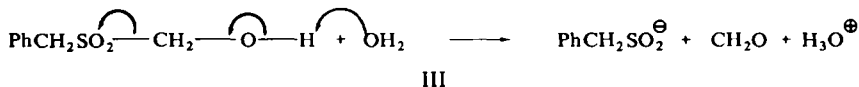
† An alternate explanation of the higher reactivity of the α -diazoketones might be hydration of the carbonyl group in the ketodiazonium ion.

‡ It cannot be excluded that the slow decomposition in neutral water proceeds partly via the thermally generated carbene.³⁴

absorbance was constant with time and the spectrum was practically identical to that of benzylnsulfonic acid in water.

Decomposition was much more rapid when I (159 mg) was dissolved in 4 ml of 60% (v/v) dioxan-water containing 0.46N HClO_4 . The reaction mixture was kept overnight at room temp and then extracted 3 times with 3 ml CH_2Cl_2 . The white crystalline material (yield 75%) obtained after removal of the solvent *in vacuo* at 25° was identical* with an authentic sample of III. The loss of about 25% can only be attributed to dissociation of III into benzylnsulfonic acid and formaldehyde.

The UV spectrum of a diluted neutral aqueous soln of III showed a max at 236 μ ($\log \epsilon$ 3.87) and the spectrum was identical within 4% to that of sodium benzylnsulfinate. Apparently III was dissociated³⁵ completely in this diluted soln into formaldehyde and benzylnsulfonic acid.† This dissociation reaction is most likely of the E-2 elimination-type:



In acidic solns in the range involved in the kinetic measurements on the α -diazosulfones (0.025–2.5N HClO_4) the products of hydrolysis showed no absorption maxima above 220 μ . These spectra were practically identical to that of benzylnsulfonic acid which is largely undissociated in these acidic solns.‡ The features of the spectra change hardly between 0.5 and 2.5N HClO_4 . In addition, the UV spectra obtained by dissolving III and benzylnsulfonic acid are identical within experimental error between 0.025 and 2.5N HClO_4 . No indications were found for disproportionation of the sulfonic acid.

In the more strongly acidic (about 2.5N) HClO_4 solns, the dissociation of III is no longer fast compared with the hydrolysis of I. In these media the absorbance at 230 μ increases again after the initial decrease (from which the rate constants of hydrolysis can be evaluated). The increase in absorbance also fits excellently first order kinetics and gives a rate constant ($k = 362 \cdot 10^{-5} \text{ sec}^{-1}$ in 2.655N HClO_4) which is within experimental error equal to that obtained from the increase in absorbance upon addition of III to a soln of the same acidity ($k = 376 \cdot 10^{-5} \text{ sec}^{-1}$). These observations can be interpreted by assuming a relatively slow dissociation³⁷ of the protonated or hydrogen bonded III. The experiments show that the sulfonic acid and formaldehyde are actually formed *via* the intermediate hydroxymethyl sulfone and not in a concerted mechanism directly from the diazonium ion.

No evidence has been found for the intermediacy of covalent perchlorates³⁸ $\text{RSO}_2\text{CH}_2\text{OClO}_3$ (which have UV spectra very different from those of the sulfonic acids RSO_2H and relatively slow rates of hydrolysis in acidic solns).§

If I (122 mg) was dissolved in 10 ml of 60% (v/v) dioxan-water containing 4.6N HCl and the reaction product was isolated by extraction with CH_2Cl_2 , 91% of pure $\text{PhCH}_2\text{SO}_2\text{CH}_2\text{Cl}$ IV (m.p. 101–102°, lit.³⁹ 103°) was obtained. No III could be detected. The UV spectrum of IV showed a max at 210 μ ($\log \epsilon$ 3.98) and a low intensity max at about 260 μ . The spectrum did not change with time in acidic soln or in neutral water. Conversion of III into IV upon treatment with HCl was impossible under the reaction conditions used for the hydrolysis of α -diazosulfones.

The composition of the reaction products of I in aqueous HCl and in HCl solns in 40% (v/v) and 60% (v/v) dioxan-water could be analysed with an accuracy of about 5% by comparison of the UV spectra with reference spectra of mixtures of III and IV of known composition.

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

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* Identical IR and PMR spectra.

† Sulfonic acids are rather strong acids.

‡ The UV spectra clearly indicated that benzylnsulfonic acid is less dissociated in D_2O than in water.

§ A study on the mechanism of the hydrolysis reaction of this type of perchloric esters is in progress in our laboratory.

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