710. *Intermediates in the Decomposition of Aliphatic Diazo-compounds. Part II.*[1] *Decomposition of Diaryldiazomethanes in Acetonitrile Catalysed by Arenesulphonic Acids.*

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Decomposition of diaryldiazomethanes in acetonitrile catalysed by arenesulphonic acids changes in kinetic form as the concentration of water in the medium is changed. At water concentrations greater than 2M, the reaction is of the first order in diazo-compound and the effects of substituents and of replacement of water by deuterium oxide on the reaction rate are consistent with rate-determining protonation of the diazo-compound. At lower water concentrations and in anhydrous acetonitrile the apparent kinetic order in diazo-compound is zero. Substituent effects, solvent isotope effects, and the effect of variation in the acid strength of the catalyst on the reaction velocity indicate that arenesulphonate esters are rapidly formed from the diazo-compound and catalyst. These esters slowly ionise to yield diarylmethyl cations. From a consideration of their proportions it is concluded that the products, tetra-arylethylene and diarylmethanol, arise by competition between the diazo-compound and water for the intermediate diarylmethyl cations in the region of both zero- and of first-order kinetics.

IN Part I[1] we showed that decomposition of diaryldiazomethanes in acetonitrile catalysed by perchloric acid yields tetra-arylethylene (and diarylmethanol when water is present) by a mechanism involving initial, rate-determining proton-transfer to the diazo-compound. Formation of tetra-arylethylene was first noticed when using toluene-*p*-sulphonic

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[1] Part I, Bethell and Callister, preceding paper.

acid as catalyst.[2] The kinetics of this reaction were not studied in detail but appeared to be complex, the kinetic order in diazo-compound apparently changing with catalyst concentration.[2b] We therefore re-examined the kinetics and mechanism of the sulphonic acid-catalysed reaction, using procedures somewhat similar to those described earlier. We conclude that the mechanism of the reaction is the same as when perchloric acid is the catalyst provided that water is present at a concentration greater than 2M. In less aqueous and in anhydrous acetonitrile the diazo-compound is apparently rapidly converted into the corresponding sulphonate ester which yields a diarylmethyl cation in the rate-determining step of the reaction. As in the earlier study, our results support the view that the nature of the products is determined by competition between the available nucleophiles for the intermediate carbonium ions, these reactions being very rapid.

EXPERIMENTAL

Materials.—*Solvents.* Acetonitrile was purified and its purity checked as previously described.[1]

Sulphonic acids. Toluene-*p*-sulphonic acid monohydrate was dried by azeotropic distillation with benzene, the anhydrous acid, m. p. 38°, crystallising from the benzene solution. Benzene sulphonic acid was a fresh commercial sample, used without purification.

p-Bromobenzenesulphonic acid was liberated when dry hydrogen chloride was passed into an ether suspension of the sodium salt, and it was obtained on evaporation of the filtered mixture; recrystallised twice from ether–light petroleum, it had m. p. 103—104°. The sulphonic acids were all stored *in vacuo* over phosphorus pentoxide. For the kinetic experiments, stock solutions of the acids (0·0025M) in anhydrous acetonitrile were prepared and diluted as required. They showed no evidence of the ageing found with acetonitrile solutions of perchloric and other mineral acids.[1,3]

Diaryldiazomethanes. These were prepared by oxidation of the corresponding benzophenone hydrazones with yellow mercuric oxide as previously described.[1] The following have not previously been reported: 4-*Chlorobenzophenone hydrazone*, plates (from aqueous ethanol), m. p. 103—104° (Found: C, 67·5; H, 4·9; N, 11·8. $C_{13}H_{11}ClN_2$ requires C, 67·7; H, 4·8; N, 12·2%). 4,4′-*Difluorobenzophenone hydrazone*, plates (from aqueous ethanol), m. p. 81—82° (Found: C, 67·6; H, 4·4; N, 12·2. $C_{13}H_{10}F_2N_2$ requires C, 67·2; H, 4·3; N, 12·1%). 4,4′-*Dinitrobenzophenone hydrazone*, yellow prisms (from ethanol), m. p. 208—209° (Found: C, 54·9; H, 3·6; N, 19·5. $C_{13}H_{10}N_4O_4$ requires C, 54·6; H, 3·5; N, 19·6%). 3-*Methylbenzophenone hydrazone* (from aqueous ethanol), m. p. 96—97° (Found: C, 80·5; H, 6·7; N, 13·4. $C_{14}H_{14}N_2$ requires C, 80·0; H, 6·7; N, 13·3%). In addition, the hydrazones of 3-bromo- and 3-methoxybenzophenone, hitherto unreported, were obtained as oils; like certain of the crystalline hydrazones, they darkened on storage.

In addition to the diazo-compounds described in Part I, those in the annexed Table have been prepared. Where possible, diazo-compounds were recrystallised until they gave reproducible rates of decomposition on treatment with toluene-*p*-sulphonic acid in anhydrous acetonitrile. The *meta*-substituted diazo-compounds, except 3,3′-dinitrodiphenyldiazomethane, we found impossible to crystallise. In such cases, however, the reproducibility of rates from different preparations of the diazo-compound was satisfactory and weighed samples

Diphenyldiazomethane derivative	M. p.	$\lambda_{max.}$ (mμ) (in MeCN)	ε
3-Bromo	Oil	530	78
4-Chloro	26—27°	526	85
4,4′-Difluoro	50—52	530	80
3-Methyl	Oil	526	81·5
3-Methoxy	Oil	526	82
3-Nitro	Oil	395	576
3,3′-Dinitro	128—129 (decomp.)	380	5,900
4,4′-Dinitro	143—144 (decomp.)	396	11,600

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[2] (*a*) Roberts and Watanabe, *J. Amer. Chem. Soc.*, 1950, **72**, 4869; Roberts, Watanabe, and McMahon, *ibid.*, 1951, **73**, 760. (*b*) Roberts, personal communication.

[3] Kolthoff, Bruckenstein, and Chantooni, *J. Amer. Chem. Soc.*, 1961, **83**, 3927.

of the compounds evolved >0·98 mol. of nitrogen on treatment with toluene-*p*-sulphonic acid in acetonitrile.

Tetra-arylethylenes. Decomposition of the diaryldiazomethanes, except those having one or more nitro-substituents, in anhydrous acetonitrile with toluene-*p*-sulphonic acid as catalyst gave the corresponding substituted tetraphenylethylene in approximately quantitative yield. The new compounds prepared in this way are tabulated.

Tetra-arylethylenes, $(R\cdot C_6H_4)PhC{:}CPh(C_6H_4R)$.

R	M. p.	$\lambda_{max.}$ (mμ) (in EtOH)	ε	Found (%) C	Found (%) H	Required (%) C	Required (%) H
m-Br	130—132°	313	13,660	63·4	3·8	63·7	3·7
p-Cl	198—199	313	12,800	77·6	4·3	77·8	4·5
m-Me	117—118	308	13,000	93·0	6·7	93·3	6·7
m-MeO	125—126	318	11,900	85·6	6·1	85·7	6·2
Tetra-*p*-F	189—190 *	300	15,700	—	—	—	—

* Lit.,[4] 189—190°.

3-Nitrodiphenyldiazomethane was also decomposed in anhydrous acetonitrile by a catalytic amount of toluene-*p*-sulphonic acid, but the olefin was not obtained when the reaction mixture was worked up in the usual way. The product, obtained in high yield, was identified as 3-nitrobenzophenone from its infrared spectrum and 2,4-dinitrophenylhydrazone. The derivative was identical with an authentic specimen, m. p. 245—246°, prepared from the pure ketone (Found: C, 56·1; H, 3·3; N, 17·4. $C_{19}H_{13}N_5O_6$ requires C, 56·0; H, 3·2; N, 17·2%).

Decomposition of the two dinitrodiphenyldiazomethanes required the stoicheiometric amount of toluene-*p*-sulphonic acid. Removal of the solvent at low temperature furnished the corresponding esters, 3,3′-, m. p. 134—135° (Found: C, 55·8; H, 3·9; N, 6·4; S, 7·6. $C_{20}H_{16}N_2O_7S$ requires C, 56·1; H, 3·8; N, 6·5; S, 7·5%), and *4,4′-dinitrodiphenylmethyl toluene-*p*-sulphonate*, m. p. 172—173° (Found: C, 56·0; H, 3·7; N, 6·5; S, 7·5%).

Diarylmethanols. In aqueous acetonitrile, hydrolysis accompanied formation of the tetra-arylethylene. The substituted diphenylmethanols were readily separated by column chromatography on alumina and compared with specimens prepared by reduction of the corresponding benzophenone. They are tabulated.

Diarylmethanols.

Subst.	3-Br	4-Cl	4,4′-F_2	3-CH_3	3-CH_3O	3-NO_2	3,3′-$(NO_2)_2$	4,4′-$(NO_2)_2$
M. p.: found	43°	62°	45—46° *	53°	41°	68—70°	106—107°	168—169°
lit. ...	43	60—61	47·3—47·5, 92—93, 34—35	52·9—53·5	41	68—71	106·5—107·5	168—169
Ref.	5	6	7*a*—*c*	8	9	10	11	12

* Found: C, 71·2; H, 4·2. Calc. for $C_{13}H_{10}F_2O$: C, 70·9; H, 4·6%.

Kinetic Procedure.—This was as previously described.[1] At water concentrations greater than 2M, the decomposition followed first-order kinetics to at least 90% completion of the reaction. When less aqueous media were used, graphs of $D_t - D_\infty$ (where D_t is the optical density of the reaction mixture at time t, measured at the absorption maximum of the diazo-compound) against t were rectilinear over the first 75% of reaction, indicating obedience to a zero-order kinetic equation. Examples of this kinetic behaviour are shown in Fig. 1. In addition, it was established that the reaction products exert no influence on the reaction rate and kinetic form; nor did added benzophenone azine which might contaminate solutions of

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[4] Johnson, Smith, Stacey, and Tatlow, *J.*, 1952, 4710.

[5] Montagne and van Charante, *Rec. Trav. chim.*, 1912, **31**, 315.

[6] Tietz and McEwen, *J. Amer. Chem. Soc.*, 1955, **77**, 4007.

[7] (*a*) Gunther and Blinn, *J. Amer. Chem. Soc.*, 1950, **72**, 4282, 5770; (*b*) Picard and Cearns, *Canad. J. Res.*, 1950, **28**, *B*, 56; (*c*) Olah, Pavlath, and Kuhn, *Acta Chim. Acad. Sci. Hung.*, 1955, **7**, 85.

[8] Berliner and Chen, *J. Amer. Chem. Soc.*, 1958, **80**, 343.

[9] Stoermer, *Ber.*, 1908, **41**, 323.

[10] Newman and Smith, *J. Org. Chem.*, 1948, **13**, 592.

[11] Deno and Schriesheim, *J. Amer. Chem. Soc.*, 1955, **77**, 3051; Stewart and Smith, *ibid.*, 1957, **79**, 5457.

[12] Curtin and Leskowitz, *J. Amer. Chem. Soc.*, 1951, **73**, 2630; Gorvin, *J.*, 1955, 83.

diazo-compounds in acetonitrile which had been stored for some time. For the decomposition of diphenyldiazomethane in anhydrous acetonitrile it was also established that the rates of disappearance of diazo-compound and of appearance of tetraphenylethylene were equal: there is thus no appreciable storage of intermediates.

Potentiometric Measurements.—Variations in the concentration of acid in the dilute acetonitrile solutions employed in the kinetic experiments could be followed by use of a glass–mercurous sulphate electrode system. This was used in preference to the more conventional calomel electrode to avoid diffusion into the reaction mixtures of chloride ions which would lead to an acid-consuming formation of diphenylmethyl chloride. A saturated methanolic solution of potassium sulphate replaced the more usual aqueous solution in the reference electrode.[13] The electrode assembly was used in conjunction with a direct-reading pH meter (E.I.L., model 23A). The apparatus was calibrated against solutions of toluene-*p*-sulphonic acid in anhydrous and in 2·22M-aqueous acetonitrile of known concentration. Plots of potential difference against the logarithm of the acid concentration were satisfactorily linear over the concentration range 4×10^{-5} to 2×10^{-3}M. The sensitivity of the method to changes in acid concentration was rather low in the aqueous solutions, and this led to difficulties in the kinetic experiments where it was required to differentiate between changes in potential due to changes in acid concentration and those due to the slight drift of potential with time (up to 5 mv during the reaction time).

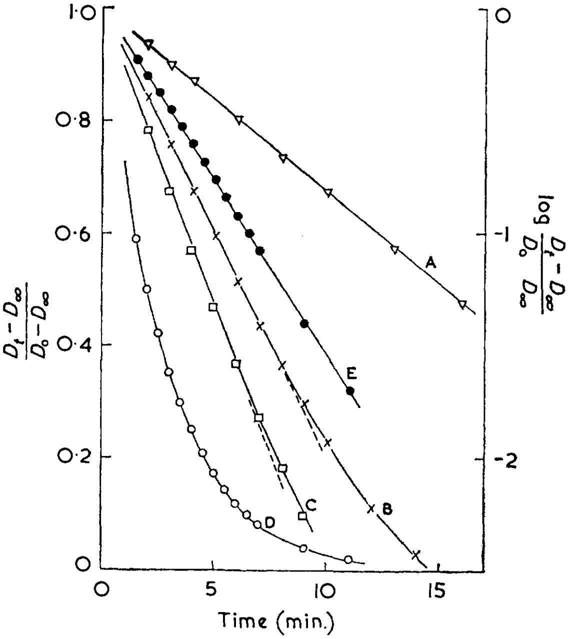

FIG. 1. Specimen zero- and first-order kinetic behaviour: (A) 4-chlorodiphenyldiazomethane, 1×10^{-3}M-toluene-*p*-sulphonic acid; (B) diphenyldiazomethane, 1×10^{-3}M-toluene-*p*-sulphonic acid; (C) diphenyldiazomethane, $2{\cdot}5 \times 10^{-4}$M-toluene-*p*-sulphonic acid, 0·66M-H_2O; (D) diphenyldiazomethane, 2×10^{-4}M-toluene-*p*-sulphonic acid, 2·22M-H_2O; (E) as (D), logarithmic scale.

Indicator measurements, product analyses, and determinations of reactivity ratios for the competition between diazo-compounds and water for reaction intermediates were as described in Part I.

RESULTS AND DISCUSSION

Ionisation of Arenesulphonic Acids in Acetonitrile.—Acetonitrile has feeble basic properties and its ability to solvate ions, particularly anions, is small.[14] These two properties render it a differentiating solvent for acids which are strong in aqueous solution. In a recent investigation, Kolthoff, Bruckenstein, and Chantooni [3] found that, of the

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[13] Miron and Hercules, *Analyt. Chem.*, 1961, **33**, 1770.

[14] Parker, *Quart. Rev.*, 1962, **16**, 163.

common mineral acids, only perchloric acid is strong in acetonitrile and that hydrobromic, sulphuric, and hydrochloric acid are only slightly dissociated.

Our investigations of the acidity of arenesulphonic acids in acetonitrile, recorded in Tables 1 and 2, are not extensive but show certain facts: (*a*) The arenesulphonic acids studied are all weak acids in acetonitrile. A measurable protonation equilibrium is established with the indicator base *m*-nitroaniline in the concentration range examined. Comparable concentrations of perchloric acid in anhydrous acetonitrile completely protonate this indicator,[1] a measurable equilibrium being attained with much less basic indicators, *e.g.*, 4-chloro-2-nitroaniline [3] (*ca.* 3·7 p*K* units less basic in aqueous solution).

TABLE 1.

Ionisation of *m*-nitroaniline (B) in solutions of *para*-substituted benzenesulphonic acids in acetonitrile.

Subst. (σ)	10^4[Ar·SO$_3$H]$_{st}$M	R *	10^4[ArSO$_3$H] †	log R − log [Ar·SO$_3$H]
Br (+0·23)	2·0	0·302	0·74	3·62
H (0·00)	2·0	0·239	1·05	3·36
Me (−0·17)	1·0	0·101	0·56	3·25
	2·0	0·192	1·23	3·19
	5·0	0·470	3·50	3·13
	10	1·042	7·55	3·14

* $R = ([BH^+] + [BH^+Ar{\cdot}SO_3^-])/[B]$. † $[Ar{\cdot}SO_3H] = [Ar{\cdot}SO_3H]_{st} - ([BH^+] + [BH^+Ar{\cdot}S_3^-])$.

TABLE 2.

Effect of added water on the ionisation of *m*-nitroaniline in solutions of toluene-*p*-sulphonic acid in acetonitrile.

[Ar·SO$_3$H]$_{st}$ 2·0 × 10^{-4}M. Indicator concn.: 4·7 × 10^{-4}M.

[H$_2$O] (M)	0·00	0·22	0·66	1·11	1·54	2·22	3·74	4·44
R	0·192	0·170	0·127	0·071	0·043	0·025	0·013	0·012
$10^{-3}R$/[Ar·SO$_3$H]	1·56	1·31	0·96	0·42	0·24	0·13	0·07	0·06

(*b*) The indicator measurements on anhydrous solutions of toluene-*p*-sulphonic acid (Table 1) are not compatible with the two modes of ionisation observed with mineral acids in acetonitrile,[3] *viz.*: $HX + B \rightleftharpoons BH^+ + X^-$; $2HX + B \rightleftharpoons BH^+ + HX_2^-$. A graph of log R against log [Ar·SO$_3$H], where [Ar·SO$_3$H] is taken to be [Ar·SO$_3$H]$_{st}$ − [BH$^+$], is linear with a slope of 0·9. Such behaviour is observed for acids ionising according to the scheme,[15] $HX + B \rightleftharpoons BH^+X^- \rightleftharpoons BH^+ + X^-$. Dissociation of the ion-pairs BH^+X^- is responsible for the deviation of the slope from unity. Our results are not sufficiently detailed to enable us to derive values for the constants governing the above equilibria. However, the quantity $([BH^+] + [BH^+X^-])/[B][HX]$, *i.e.*, R/Ar·SO$_3$H, under comparable conditions should give an approximate measure of the strength of the acid. The results in Table 1 show that for benzene-, *p*-bromobenzene-, and toluene-*p*-sulphonic acid the values of this quantity are in the ratio 1 : 1·8 : 0·7. Thus substituents in the benzene ring appear to affect the strengths of benzenesulphonic acids in the same way as they affect those of benzoic acids (cf. the σ-values in Table 1).

(*c*) Addition of water to solutions of toluene-*p*-sulphonic acid in acetonitrile reduces the extent of protonation of *m*-nitroaniline. A similar effect has been observed with solutions of perchloric acid in acetonitrile,[1] and the phenomenon appears to be general for acid solutions in solvents less basic than water. The usual explanation is in terms of progressive replacement of protonated solvent by hydroxonium ion as the proton-transfer agent as the water concentration increases.

Arenesulphonic acids in acetonitrile solution thus behave very much like toluene-*p*-sulphonic acid in glacial acetic acid. Measurements of the strength of toluene-*p*-sulphonic acid in the latter solvent have shown [15] that it is slightly stronger than hydrochloric acid,

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[15] Kolthoff and Bruckenstein, *J. Amer. Chem. Soc.*, 1956, **78**, 1.

confirming earlier, less precise conclusions based on conductivity measurements and catalytic activities as well as indicator measurements.[16] The weakness of the sulphonic acids coupled with the fact that ion association appears to be important in acetonitrile (cf. Iliceto *et al.*[17]) probably explain the stability of solutions of these acids in acetonitrile.

Kinetics and Mechanism of the Decomposition of Diaryldiazomethanes in Acetonitrile Catalysed by Arenesulphonic Acids.—In most of the experiments the catalyst was toluene-*p*-sulphonic acid. The kinetic results are recorded in Tables 3—7. As mentioned above, a change in the kinetic form of the decomposition occurs when the concentration of water in the reaction medium is varied (see Fig. 1). It is convenient therefore to divide the discussion into two sections, dealing with the decomposition first in acetonitrile containing water at a concentration greater than 2M and then in less aqueous media.

TABLE 3.

Rates of decomposition of diphenyldiazomethane in acetonitrile catalysed by toluene-*p*-sulphonic acid (HOTs) at 29·5°.

10^4[HOTs] (M)	0·5	1·0	1·5	2·0	2·0	2·0	2·0	2·0
10^2[Ph_2CN_2] (M)	1·60	1·65	1·58	0·23	0·30	0·38	0·48	0·96
10^5k_0 (mole l.$^{-1}$ min.$^{-1}$)	7·2	13·8	17·4	25	25	27	25	27
10^4[HOTs] (M)	2·5	2·5 *	2·5 †	4·0	5·0	10·0		
10^2[Ph_2CN_2] (M)	1·61	1·35	1·32	1·59	1·54	1·58		
10^5k_0 (mole l.$^{-1}$ min.$^{-1}$)	32	84	392	53	63	128		

* Benzenesulphonic acid as catalyst. † *p*-Bromobenzenesulphonic acid as catalyst.

TABLE 4.

Effect of water on the kinetics and products of decomposition of diphenyldiazomethane catalysed by toluene-*p*-sulphonic acid in acetonitrile at 29·5°. [Ph_2CN_2]$_0$ ~ 0·014M.

			$k_{obs.}$ (mole l.$^{-1}$ min.$^{-1}$ or min.$^{-1}$)			Tetraphenylethylene (%)		
[H_2O] (M)	10^4[HOTs] (M)	Kinetic order	H_2O	D_2O	Ratio	H_2O	D_2O	r_H
0·14	2·5	0	0·00048	—	—	59	—	20
0·22	2·5	0	0·00064	0·00052	1·22	50	48	18·7
,,	4·0	0	0·00100	—	—	49	—	18
,,	2·0	0	0·00700 *	—	—	55 *	—	23·$_5$ *
0·66	2·5	0	0·00152	0·00120	1·26	28	26	20
1·11	2·5	0	0·0034	0·00216	1·26	18	16	18·$_3$
1·80	2·5	0	0·0059	0·0029	2·03	13	13	20
2·22	1·0	1	0·167	0·0734	2·28	—	—	—
,,	2·0	1	0·345	0·152	2·27	11	11	18
,,	4·0	1	0·697	—	—	—	—	—
3·33	1·0	1	0·078	—	—	7	—	19
4·44	1·0	1	0·052	0·0206	2·52	7	7	31
11·1	1·0	1	0·029	—	—	5	—	—

* 0·05M-Lithium perchlorate present.

Media containing more than 2M-*water*. Under these conditions the experimental findings are closely similar to those for anhydrous and aqueous solution of perchloric acid in acetonitrile.[1] The results of the present work may be summarised as follows: (*a*) The reaction is of the first order in both diazo-compound and acid catalyst. (*b*) Increasing the water concentration decreases the reaction rate in a similar fashion to the effect on the extent of protonation of *m*-nitroaniline. (*c*) Solvent isotope effects, k^{H_2O}/k^{D_2O}, for all the diazo-compounds examined were between 2 and 3. The effects are rather

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[16] Hantzsch and Langbein, *Z. anorg. Chem.*, 1932, **204**, 193; Hammett and Deyrup, *J. Amer. Chem. Soc.*, 1932, **54**, 4239.

[17] Iliceto, Fava, Mazzucato, and Rossetto, *J. Amer. Chem. Soc.*, 1961, **83**, 2729.

TABLE 5.

Effect of ethanol on the kinetics and products of decomposition of diphenyldiazomethane catalysed by toluene-*p*-sulphonic acid in acetonitrile at 29·5°.

Catalyst concn.: 2·5 × 10^{-4}M. $[Ph_2CN_2]_0$ ~0·014M.

$[C_2H_5 \cdot OH]$ (M)	Kinetic order	$k_{obs.}$(mole l.$^{-1}$ min.$^{-1}$ or. min^{-1})	Tetraphenylethylene (%)	r_H'
0·34	0	0·00075	15	4·3
0·69	0	0·00143	10	5·3
1·03	0	0·00249	8	6·1
1·38	0	0·00350	6	5·5
2·41	0	0·0064	4	—
3·44	0	0·0084	4	—
5·50	1	0·595	4	—
10·3	1	0·110	3	—

TABLE 6.

Rates of decomposition of substituted diphenyldiazomethanes catalysed by toluene-*p*-sulphonic acid (HOTs) in acetonitrile at 29·5°.

$[Ar_2CN_2]_0$ ~0·014M.

			$k_{obs.}$ (mole l.$^{-1}$ min.$^{-1}$ or min.$^{-1}$)		
10^4[HOTs] (M)	$[H_2O]$ (M)	Kinetic order	H_2O (or dry)	D_2O	Ratio
		3-Bromo-			
10	—	0	0·000027	—	—
100	—	0	0·000242	—	—
2·0	1·11	0	0·000137	—	—
,,	2·22	1	0·0607	0·0256	2·37
,,	3·35	1	0·0713	—	—
,,	4·44	1	0·0552	0·0190	2·91
		4-Chloro-			
2·5	—	0	0·000129	—	—
10	—	0	0·000488	—	—
2·0	0·22	0	0·000169	—	—
,,	1·11	0	0·00131	—	—
,,	2·22	1	0·205	0·0834	2·46
,,	3·33	1	0·116	—	—
,,	4·44	1	0·0695	—	—
		4,4′-Dichloro-			
2·5	—	0	0·000036	—	—
5·0	—	0	0·000072	—	—
10	—	0	0·000138	—	—
1·0	0·20	0	0·0000253	—	—
2·0	1·10	0	0·000415	—	—
,,	2·20	1	0·0810	0·0406	2·00
,,	3·35	1	0·0598	—	—
,,	4·44	1	0·0368	—	—
		4,4′-Difluoro-			
2·5	—	0	0·00078	—	—
5·0	—	0	0·00150	—	—
10	—	0	0·00291	—	—
1·0	0·22	0	0·00041	—	—
		4,4′-Difluoro-			
2·0	1·11	0	0·00108	—	—
,,	2·22	1	0·210	0·0764	2·75
,,	3·33	1	0·0782	—	—
,,	4·44	1	0·0616	—	—
		4,4′-Dimethyl-			
0·10	—	0	0·00432	—	—
		3,3′-Dinitro-			
10	2·22	1	0·0034	—	—
		3-Methoxy-			
2·5	—	0	0·00022	—	—
10	—	0	0·00095	—	—
2·0	0·22	0	0·00040	—	—
,,	1·11	0	0·00138	—	—
,,	2·22	1	0·265	—	—
,,	3·33	1	0·175	—	—
,,	4·44	1	0·135	—	—
		3-Methyl			
2·5	—	0	0·00081	—	—
5·0	—	0	0·00160	—	—
10	—	0	0·00294	—	—
2·0	0·23	0	0·00100	—	—
,,	1·11	0	0·0044	—	—
,,	2·22	1	0·451	0·200	2·26
,,	3·33	1	0·193	—	—
,,	4·44	1	0·182	—	—
		3-Nitro-			
2·0	2·22	1	0·00724	—	—

smaller than those observed for the perchloric acid-catalysed reaction. (*d*) The reaction rate is increased by increasing electron-release from substituents in the diazo-compound. (*e*) The values of the reactivity ratio r_x (the ratio of rate constants for the reaction of the diazo-compound and water with a hypothetical reactive intermediate) for a number of diazo-compounds are almost identical with values determined for perchloric acid-catalysed reactions. The exception is diphenyldiazomethane for which a value approximately half that observed in the presence of perchloric acid has been unaccountably determined.

TABLE 7.

Salt effects on the decomposition of diphenyldiazomethane catalysed by toluene-*p*-sulphonic acid (HOTs) in anhydrous acetonitrile at 29·5°.

[Catalyst]: 2·5 × 10^{-4}M.

(*a*) *Lithium perchlorate*						
10^2[$LiClO_4$] (M)	0·0	0·59	1·20	2·95	5·10	10·0
$10^3 k_{obs.}$ (mole $l.^{-1}$ $min.^{-1}$)	0·32	1·35	2·32	4·31	5·81	8·50
(*b*) *Benzyltrimethylammonium toluene*-p-*sulphonate*						
10^2[R_4NOTs] (M)	0·0	0·102	0·255	1·02	2·55	5·10
10^4 × Initial rate (mole $l.^{-1}$ $min.^{-1}$)	3·20	2·65	2·40	1·48	1·10	0·96

TABLE 8.

Olefin yields (q%) and reactivity ratios (r_X) for toluene-*p*-sulphonic acid-catalysed decomposition of (p-X·C_6H_4)$_2$$CN_2$ in aqueous acetonitrile at 29·5°.

[(p-X·C_6H_4)$_2$$CN_2$]$_0$ ~1·4 × 10^{-2}M; [Catalyst] 2·5 × 10^{-4}M.

X =	Cl		Me		MeO	
[H_2O] (M)	q	r_{Cl}	q	r_{Me}	q	r_{MeO}
0	99	—	99	—	100	—
0·22	40	11·5	$89{\cdot}_4$	385	$98{\cdot}_4$	3100
0·66	—	—	$76{\cdot}_6$	340	96	3000
1·11	12	15	67	310	$94{\cdot}_5$	3200
2·22	10	16	52	300	$91{\cdot}_4$	3200
4·44	5	16	32	290	—	—
	Av.	$14{\cdot}_6$	Av.	32_5	Av.	31_{25}

We conclude, therefore, that the mechanism of the reaction in these aqueous solutions involves rate-determining protonation of the diazo-compound, as in the perchloric acid-catalysed decomposition. Indeed, the rates of the latter reactions are only slightly (~15%) greater than those of the toluene-*p*-sulphonic acid-catalysed decompositions at the same acid concentration, suggesting that proton transfer is largely from the hydroxonium ion. The rather lower solvent isotope effects observed in the present investigation may be due to ion association which would reduce solvation of the proton transfer agent by water molecules.

The effect of substituents in the diazo-compound on the rate of decomposition catalysed by toluene-*p*-sulphonic acid, which appears to be very similar to that observed for catalysis by perchloric acid (cf. the ratio of rate constants for diphenyldiazomethane and the 4,4′-dichloro-compound in the two series) deserves further comment. In acetonitrile containing 2·22M-water, log $k_{obs.}$/[HOTs] for the various substituted diphenyldiazomethanes correlates well with the σ-values for the substituents. The slope of the regression line (ρ) is —1·991 with standard deviation 0·168 and correlation coefficient 0·986. Correlation with the σ^+-values of Brown [18] is slightly better: ρ = —2·006 with standard deviation

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[18] Brown in " Steric Effects in Conjugated Systems," ed. Gray, Butterworths, London, 1958, p. 100.

0·128 and correlation coefficient 0·992. However, results are not available for substituents for which σ^+ deviates from σ sufficiently to provide a clear-cut distinction between the two measures of the polar effect of substituents. Our observation than carefully purified 4,4′-difluorodiphenyldiazomethane always decomposes more slowly that the unsubstituted diazo-compound at the same acid concentration in the region of first-order kinetics makes us favour correlation with σ ($\sigma_{p\text{-F}} = +0{\cdot}062$; $\sigma_{p\text{-F}}{}^+ = -0{\cdot}073$).

We formulate the decomposition of diaryldiazomethanes catalysed by toluene-*p*-sulphonic acid in acetonitrile containing more than 2M-water thus:

$$\mathrm{Ar_2CN_2 + SH^+ \xrightarrow[Slow]{} Ar_2CH{\cdot}N_2^+ \xrightarrow[Fast]{} N_2 + Ar_2CH^+ \xrightarrow[Fast]{Ar_2CN_2,H_2O} Ar_2C{:}CAr_2 + Ar_2CH{\cdot}OH}$$

(S = Solvent molecule)

Media containing less than 2M-*water*. Progressive reduction of the water concentration in solutions of toluene-*p*-sulphonic acid in acetonitrile does not lead to a corresponding increase in the rate of decomposition of diaryldiazomethanes as was observed in the perchloric acid-catalysed reaction. Instead, the initial decomposition rate attains a maximum at approximately 2M-water after which the rate drops sharply and the kinetic form changes, the kinetic order of the reaction in diazo-compound becoming zero. In contrast to the perchloric acid-catalysed decomposition, reaction rates in anhydrous acetonitrile are highly reproducible and the experimental investigation was accordingly directed towards elucidation of the mechanism of the reaction with no added water.

The results of the kinetic investigation are detailed in Tables 3—7 and may be summarised as follows: (*a*) The reaction rate is proportional to the concentration of the sulphonic acid but independent of the concentration of the diazo-compound. Nevertheless, the nature of the diazo-compound affects the reaction rate. We thus have an example of pseudo-zero-order kinetics. (*b*) Addition of small amounts of water increases the rate of decomposition although added water reduces the ability of the solvent–catalyst system to protonate *m*-nitroaniline. The kinetic form is not affected by small additions of water. The solvent isotope effect $k^{\mathrm{H_2O}}/k^{\mathrm{D_2O}}$ (observed) in media containing small amounts of water (up to 1·11M) is in the range 1·2—1·3, much lower than that observed in the region of first-order kinetics. Added ethanol has a rate-enhancing effect similar to, though smaller than, that of water. However, the maximum decomposition rate is achieved at a higher concentration of hydroxylic component (*ca.* 5M) and is somewhat higher than the maximum rate attained in the presence of added water. (*c*) The reaction rate in anhydrous acetonitrile is increased by electron-releasing substituents and decreased by electron-attracting substituents. It is more sensitive to the electronic effect of substituents than the reaction in the more aqueous solutions of toluene-*p*-sulphonic acid dealt with above: log $k_{\text{obs.}}$/[HOTs] yields an excellent linear correlation with the σ^+-values of the substituents: the slope of the line, ρ, is $-4{\cdot}054$, the standard deviation from the regression line being 0·109 and the correlation coefficient 0·997. (*d*) The rate of decomposition of diphenyldiazomethane in anhydrous acetonitrile is very sensitive to the presence of added salts. Lithium perchlorate causes a marked acceleration of the reaction. The effect is non-linear, being most marked at low concentrations and levelling off as the salt concentration is increased. Added benzyltrimethylammonium toluene-*p*-sulphonate, on the other hand, reduces the rate of decomposition of diphenyldiazomethane and causes the kinetic order in diazo-compound to approach unity. Again the effect is non-linear, the rate of decomposition being changed relatively little at salt concentrations greater than 0·025M.

It is evident that the mechanism of decomposition of diaryldiazomethanes in anhydrous acetonitrile catalysed by toluene-*p*-sulphonic acid differs from that of the decomposition in more aqueous media. The salient feature is the change in kinetic form. The only satisfactory explanation of the pseudo-zero-order kinetics is to be found in a rapid initial reaction of the catalyst with the diazo-compound to yield an intermediate which decomposes slowly to give the reaction products, *viz.*:

$$\mathrm{HOTs} + \mathrm{Ar_2CN_2} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} \text{Intermediate (I)} \xrightarrow{k_b} \text{Products}$$

the concentration of intermediate (I) is then given by

$$[\mathrm{I}] = [\mathrm{HOTs}][\mathrm{Ar_2CN_2}]k_a/k_{-a}, \qquad (1)$$

and the observed rate of decomposition by

$$v = k_b[\mathrm{I}] = [\mathrm{HOTs}][\mathrm{Ar_2CN_2}]k_a k_b/k_{-a}. \qquad (2)$$

Now the actual catalyst concentration [HOTs] is related to the stoicheiometric acid concentration $[\mathrm{HOTs}]_{st}$ by the relation

$$[\mathrm{HOTs}] = [\mathrm{HOTs}]_{st} - [\mathrm{I}] \qquad (3)$$

Combination of equations (1), (2), and (3) gives the complete kinetic equation:

$$v = \frac{k_b k_a}{k_{-a}} \cdot [\mathrm{HOTs}]_{st} \cdot \frac{[\mathrm{Ar_2CN_2}]}{1 + [\mathrm{Ar_2CN_2}]k_a/k_{-a}}. \qquad (4)$$

Now, if $(k_a/k_{-a})[\mathrm{Ar_2CN_2}] \gg 1$, the catalyst concentration will be reduced almost to zero and equation (4) reduced to

$$v = k_b[\mathrm{HOTs}]_{st}.$$

Confirmation that this situation exists in anhydrous acetonitrile comes from potentiometric measurements of the acid concentration during the decomposition of diphenyldiazomethane catalysed by 2×10^{-4}M-toluene-*p*-sulphonic acid. In Fig. 2, the concentration of acid is plotted as a function of the percentage decomposition of the diazo-compound (measured spectrophotometrically) in anhydrous and 2·22M-aqueous acetonitrile. In the latter case, relatively little change in acid concentration occurs, as is to be expected for a reaction involving rate-determining proton-transfer. The upward trend in the concentration shown in Fig. 2 is almost certainly due to a small drift in potential with time independent of changes in acid concentration. Indeed, the change of potential over the period of the reaction was only 7 mv. In contrast, under anhydrous conditions, addition of diphenyldiazomethane to the catalyst solution leads to a rapid drop in the acid concentration which, after a few seconds, achieves a steady level, ~2% of the initial concentration.

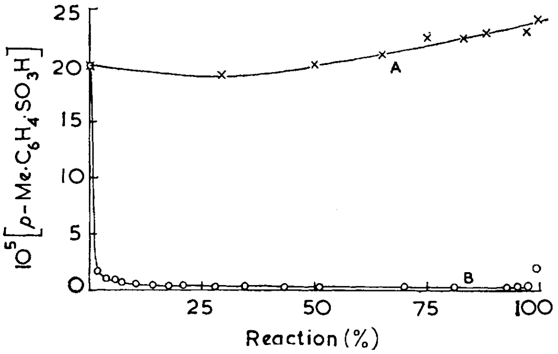

FIG. 2. Variation of free toluene-*p*-sulphonic acid concentration during decomposition of diphenyldiazomethane in acetonitrile solution: (A) 2·22M-H_2O present; (B) anhydrous conditions.

Note. Plot B. The increase in concentration towards 100% reaction is real, and the line should have been drawn to pass through the last point. ED.

This low concentration is maintained until the reaction is about 98% complete; then the concentration begins to rise again slowly. The slow rise in acid concentration continues after all the diazo-compound has decomposed but never reaches the initial level. Our explanation of the pseudo-zero-order kinetics thus seems satisfactory. The nature of the intermediate (I) remains to be determined.

The excellent correlation of log ($k_{\text{obs.}}/[\text{HOTs}]_{\text{st}}$) with σ^+ for the reaction in anhydrous acetonitrile indicates that in the transition state of the reaction an electron-deficient (carbonium) centre is formed with which *para*-substituents in the diphenyldiazomethane can conjugate directly. Thus the intermediate must be capable of yielding a diarylmethyl cation. The two simplest formulations of (I) are as follows: (*a*) Diarylmethyldiazonium ion. The formation of such an intermediate is presumed to be the first step in the mechanism of decomposition in more aqueous solutions of toluene-*p*-sulphonic acid in acetonitrile. It is not unreasonable that it should be formed under anhydrous conditions too. (*b*) Diarylmethyl arenesulphonate. Isolation of sulphonate esters in the decomposition of the two dinitrodiphenyldiazomethanes suggests that rapid formation of esters might occur generally as the first step in the formation of tetra-arylethylenes. Unlike protonation, ester formation is irreversible, *i.e.*, $k_{-\text{a}} = 0$.

Formulation (*b*) is preferred because of the considerable rate increase on changing the catalyst from toluene-*p*-sulphonic acid to the more strongly acidic benzenesulphonic or *p*-bromobenzenesulphonic acid. If the intermediate were the diazonium ion then the change of catalyst should have relatively little effect on the decomposition rate of a given diazo-compound. Even with toluene-*p*-sulphonic acid, the protonation pre-equilibrium would have to lie well on the side of the diazonium ion in order to explain the kinetic form; stronger acids could, therefore, only increase the decomposition rate by a small fraction. On the other hand, according to formulation (*b*), the nature of the sulphonic acid determines the nature of the leaving group in the rate-determining formation of the carbonium ion. Aliphatic *p*-bromobenzenesulphonates are well known to ionise more rapidly (usually by a factor of about 4 in hydroxylic solvents) than toluene-*p*-sulphonates.[19] The results of Table 3 show that use of benzenesulphonic acid in place of toluene-*p*-sulphonic acid increases the rate of decomposition of diphenyldiazomethane by a factor of 2·6, while use of *p*-bromobenzenesulphonic acid brings about a 12-fold acceleration.* These more pronounced effects probably arise from the different anion solvation relations obtaining in dipolar aprotic solvents compared with solvents capable of hydrogen bonding.[14]

The value of ρ for the toluene-*p*-sulphonic acid-catalysed decomposition of substituted diphenyldiazomethanes, —4·05, is very close to those derived by Okamoto and Brown [20] for the unimolecular solvolysis of substituted diphenylmethyl halides in ethanol (—4·05), propan-2-ol (—4·06), and 7 : 3 acetone–water (—4·11). This is strongly indicative of similar transition states in the two types of reaction. The effect of two nitro-substituents is thus readily understandable. Zero-order kinetics are observed when $k_{\text{a}} \gg k_{-\text{a}}, k_{\text{b}}$. However, if k_{b} is very small, there will be no regeneration of the catalyst and the reaction will stop at the intermediate stage. The powerful electron-attracting effect of nitro-groups would be expected to reduce the ionisation rate of the intermediate ester drastically.

The parallelism between solvolysis of alkyl halides and sulphonic acid-catalysed decomposition of diaryldiazomethanes extends to the variation of reaction rate with concentration of water. In the region of zero-order kinetics, addition of water, besides causing the appearance of diarylmethanol in the products, increases the velocity constant. The effect is linear in the concentration of water up to about 0·5M, whereafter the rate

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* The effect of changing *para*-substituent in the benzenesulphonic acid catalyst on the rate of decomposition of diphenyldiazomethane agrees well with the electronic effect of the substituent as measured by σ. The value of ρ is 2·7.

[19] See, *e.g.*, Winstein, Clippinger, Fainberg, Heck, and Robinson, *J. Amer. Chem. Soc.*, 1956, **78**, 328.

[20] Okamoto and Brown, *J. Org. Chem.*, 1957, **22**, 485.

rises more sharply. Identical behaviour has been observed by Gelles, Hughes, and Ingold[21] for the hydrolysis of t-butyl bromide in nitromethane. These authors also observed that the rate-enhancing effect of water was greater than that of ethanol but less than that of phenol. This is the order of acidity of the hydroxyl compounds and led the authors to attribute the kinetic effect to electrophilic catalysis of ionisation. We have observed analogous behaviour in the present investigation: ethanol was less effective than water (at the same concentration) in increasing the decomposition rate. The value of the reactivity ratio, $r_H'(\equiv k_H^{Ph_2CN_2}/k_H^{C_2H_5 \cdot OH})$, calculated from the ratio of the products of decomposition of diphenyldiazomethane, was much less than r_H and yielded a value of $k_H^{C_2H_5 \cdot OH}/k_H^{H_2O}$ of approximately 4. Thus the overall decomposition rate is increased by added hydroxylic compounds in the order of their acidities, but the products are determined by processes in which ethanol is more reactive than water, *i.e.*, the order of nucleophilic activity. This provides further confirmation that the rate- and the product-determining step of the reaction are separate.

The effects of added salts on the rate of the toluene-*p*-sulphonic acid-catalysed decomposition of diphenyldiazomethane indicate that the unimolecular decomposition of the intermediate ester is more complex than its formal representation. The rate reduction and trend towards first-order kinetics as the concentration of benzyltrimethylammonium toluene-*p*-sulphonate is increased has the appearance of a common-ion effect. The non-linearity of the effect on the rate of reaction suggests that solvolysis of the sulphonate ester may involve ion-pair intermediates whose concentration is not affected by added common ions. In the same way, the marked, non-linear accelerating effect of added lithium perchlorate is similar qualitatively, though not in magnitude, to the effect on the rate of acetolysis of toluene-*p*-sulphonate esters observed by Winstein and his co-workers, and attributed by them to anion exchange in solvent-separated ion pairs.[22] A satisfactory explanation of the present results awaits a more detailed study of kinetic salt effects in dipolar aprotic solvents.

The reactivity ratios, r_X, observed in the region of zero-order kinetics are the same, within the experimental error, as those determined in media containing more than 2M-water. Evidently the intermediate for which the available nucleophiles compete is the same at all water concentrations. Since we have demonstrated that in the zero-order case loss of nitrogen precedes the rate-determining step, this intermediate must be in all cases the diarylmethyl cation. We can, however, offer no explanation for the halving of the reactivity ratio observed in the decomposition of diphenyldiazomethane catalysed by toluene-*p*-sulphonic acid compared with that for the perchloric acid catalysed-reaction. The presence of lithium perchlorate in a reaction mixture containing toluene-*p*-sulphonic acid as the catalyst led to a reactivity ratio slightly higher than that observed when no salt was added. The salt concentration was, however, much higher than the concentration of perchloric acid used in the experiments described in Part I and its effect may be explained if ionic solvation binds water molecules preferentially and thus reduces the water activity in the body of the reaction solution.

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[21] Gelles, Hughes, and Ingold, *J.*, 1954, 2918.

[22] Winstein, Klinedinst, and Robinson, *J. Amer. Chem. Soc.*, 1961, **83**, 885.