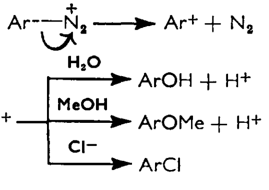
721. *Poly-*(m*-aminostyrene) and the Copolymer with Styrene. Kinetics of the Decomposition of Poly-*(m*-styrenediazonium Chloride) and Related Diazonium Chlorides.*

By C. L. ARCUS and A. HALLIWELL.

Poly-(*m*-aminostyrene) and a 2 : 1 styrene–*m*-aminostyrene copolymer have been prepared. The polymeric and copolymeric amines have been diazotised, and the rates of decomposition of the resultant diazonium chlorides, and of benzene- and cumene-*m*-diazonium chloride, in aqueous methanol at 29·8° have been determined. All are of the first order and have constants respectively 3·47, 3·10, 1·14, and 7·15 × 10^{-4} sec.$^{-1}$. From comparison of these rates it is inferred that, in the decomposition of the polymeric and copolymeric diazonium cations, the polyvinyl main chain releases electrons towards the benzenediazonium side-groups.

IN order to add to data on the reactivity of groups attached to macromolecules, we have prepared, and studied the decomposition of, polymeric diazonium salts derived from *m*-aminostyrene.

The decomposition of benzene- and alkylbenzene-diazonium chlorides closely follows first-order kinetics;[1,2,3] even in such concentrated aqueous solution that the molar ratio of water to benzenediazonium chloride is 2·36 : 1 the decomposition is of first rather than of second order.[2] From a consideration of evidence in the literature, Waters[4] proposed a unimolecular rate-determining decomposition (1) of the arenediazonium cation, followed by rapid attack on the solvent, water (2); and DeTar and Sagmanli,[5] who cite further results, point out that other nucleophilic agents, such as methanol and chloride ion, may also react (3, 4).



$$\mathrm{Ar{-}\overset{+}{N}_2 \longrightarrow Ar^+ + N_2} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\mathrm{Ar^+ \xrightarrow{H_2O} ArOH + H^+} \quad \ldots\ldots\ldots\ldots \quad (2)$$

$$\mathrm{Ar^+ \xrightarrow{MeOH} ArOMe + H^+} \quad \ldots\ldots\ldots\ldots \quad (3)$$

$$\mathrm{Ar^+ \xrightarrow{Cl^-} ArCl} \quad \ldots\ldots\ldots\ldots \quad (4)$$

The rate of decomposition of aqueous benzenediazonium chloride is insensitive to changes in acidity. The results of Moelwyn-Hughes and Johnson[1] show that when water is replaced by 0·41N-hydrochloric acid as the initial solvent, the rate constant at 60·1° increases by 7%, and those of Crossley, Kienle, and Benbrook[2] that a similar alteration from 0·02 to 0·1N-hydrochloric acid results in a 3% increase at 35·0°.

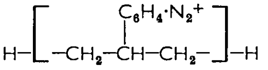
---

[1] Moelwyn-Hughes and Johnson, *Trans. Faraday Soc.*, 1940, **36**, 948.
[2] Crossley, Kienle, and Benbrook, *J. Amer. Chem. Soc.*, 1940, **62**, 1400.
[3] Lewis and Miller, *J. Amer. Chem. Soc.*, 1953, **75**, 429.
[4] Waters, *J.*, 1942, 266.
[5] DeTar and Sagmanli, *J. Amer. Chem. Soc.*, 1950, **72**, 965.

From the above it was inferred, as a premise of the work now reported, that decomposition of a diazonium cation is essentially a unimolecular reaction not readily perturbed by alteration in the acidity of the medium; whence, were any unusual feature of rate or order to be encountered in the decomposition of a polymeric diazonium salt, it could probably be ascribed to a peculiarity of the reactivity of macromolecules.

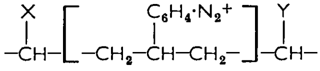
Recorded data, discussed below, indicate that the effect of *m*-alkyl substituents on the rate of decomposition of benzenediazonium chloride is accounted for by the inductive electron-release of those groups, but that this is not so for *p*-alkyl substituents. For this reason polymers and copolymers of *m*-aminostyrene have been selected for investigation.

It was considered that special characteristics, due to the attachment of the diazonium groups to a macromolecule, could be assessed by comparison of the kinetics of decomposition with those for benzenediazonium chloride, representing the individual side-group, and cumene-*m*-diazonium chloride, representing the side-group together with the chain carbon atom to which it is combined and the two adjacent atoms [compare bracketed structures (I) and (II)]. Further, in certain reactions of groups attached to macromolecules, the interaction of neighbouring side-groups is important; to evaluate this factor in the present reaction, 2 : 1 copolymers of styrene and *m*-aminostyrene have been prepared; here the benzenediazonium groups in the diazotised copolymers are on average separated by two benzene rings, whereby possible interaction of the former groups is much reduced.



$$\mathrm{H{-}\left[{-}CH_2{-}\overset{\displaystyle C_6H_4{\cdot}N_2^+}{\overset{|}{C}H}{-}CH_2{-}\right]{-}H}$$

(I)



$$\mathrm{\overset{\displaystyle X}{\overset{|}{{-}C}H}{-}\left[{-}CH_2{-}\overset{\displaystyle C_6H_4{\cdot}N_2^+}{\overset{|}{C}H}{-}CH_2{-}\right]{-}\overset{\displaystyle Y}{\overset{|}{C}H}{-}}$$

(II)

EXPERIMENTAL

M. p.s are corrected. Unless otherwise stated, hydrochloric acid refers to 11·73N-acid.

Aniline hydrochloride, recrystallised from ethanol and dried at 5 mm. over phosphoric oxide, had m. p. 200·5—201° (Found: Cl, 27·35. Calc. for C_6H_8ClN: Cl, 27·35%).

m-*Cumidine Hydrochloride*.—A mixture of nitric acid (*d* 1·42; 100 g.) and sulphuric acid (*d* 1·84; 200 g.) was cooled to $-10°$ and added dropwise with stirring in 3 hr. to cumene (b. p. 149·5—152·5°; 101 g.), kept at 0—5° by an ice–salt bath and by addition of solid carbon dioxide. After being stirred for a further hour, the whole was poured on ice and extracted with ether. The extract was washed with water, dried (K_2CO_3), and evaporated. On fractionation at 15 mm. through a heated 30 cm. Vigreux column, fractions totalling 115 g. of 4-nitrocumene, $n_D^{25} \nless 1{\cdot}531$, were obtained. It (290 g.) was hydrogenated (cf. Gilman *et al.*[6]) in 96% ethanol (100 ml.) with Raney nickel (B.D.H. stabilised; 4·5 g.); the maximum temperature and pressure were 129° and 75 atm., the autoclave being allowed to cool overnight. The contents were poured into water (3 l.) and extracted with ether; the extract was dried (K_2CO_3) and evaporated. The product yielded *p*-cumidine (185 g.), b. p. 102—104°/8 mm., n_D^{25} 1·5422. Acetylation, according to Haworth and Barker's directions,[7] gave *N*-acetyl-*p*-cumidine, m. p. 104—104·5°.

This compound (28·3 g.) was added in 30 min. to a mixture of nitric acid (d_4^{28} 1·487; 30 g.), acetic acid (recrystallised; 85 g.), and acetic anhydride (65 g.) at 5—10°. It was so maintained for a further 2 hr. with occasional stirring, then poured into iced water. The product was filtered off, washed free from acid with water, and allowed to air-dry, then extracted with boiling light petroleum (b. p. 60—80°). The material from evaporation of the extract, recrystallised from 70% ethanol, yielded 4-isopropyl-2-nitroacetanilide (23·0 g.), m. p. 79·5—80°.

The nitration also yielded ~3% of a compound, insoluble in the light petroleum, having, after recrystallisation from ethanol, m. p. 216·5—217°. Carpenter, Easter, and Wood [8] suggest that it is 4-*isopropyl*-2,6-*dinitroacetanilide* and this has been verified by analysis (Found: N, 15·8. $C_{11}H_{13}N_3O_5$ requires N, 15·7%). The compound was refluxed for 80 min. with hydrochloric acid and ethanol; the whole was cooled and made alkaline; the product, recrystallised from

---

[6] Gilman, Avakian, Benkeser, Broadbent, Clark, Karmas, Marshall, Massie, Shirley, and Woods, *J. Org. Chem.*, 1954, **19**, 1072.

[7] Haworth and Barker, *J.*, 1939, 1302.

[8] Carpenter, Easter, and Wood, *J. Org. Chem.*, 1951, **16**, 589.

benzene containing a little methanol, yielded 4-isopropyl-2,6-dinitroaniline, m. p. 149·5—150°. The above authors, who obtained the amine by alkaline hydrolysis, record m. p. 149—149·5°.

4-Isopropyl-2-nitroacetanilide was hydrolysed by the method of Carpenter *et al.*;[8] the amine, which when recrystallised from aqueous ethanol had m. p. 35·5°, was at once reduced. To a solution of 4-isopropyl-2-nitroaniline (from 67·1 g. of the acetyl derivative) in hydrochloric acid (140 ml.) and 96% ethanol (150 ml.) at 0° to −5°, sodium nitrite (21·0 g.) in water (50 ml.) was added in 30 min. The mixture was kept at 0—5° for 2½ hr., during the last 30 min. of which 50% hypophosphorous acid (170 ml.), cooled to 0°, was added (cf. Gilman *et al.*[6]). The whole was kept at 5° for 90 hr., then steam-distilled. The distillate was extracted with ether, and the extract dried (K_2CO_3) and evaporated, yielding 3-nitrocumene (33·5 g.), b. p. 70·5—71°/0·5 mm., n_D^{25} 1·5292.

This compound (34·0 g.), hydrated stannous chloride (215 g.), hydrochloric acid (143 ml.), and 96% ethanol (70 ml.) were heated for 15 min., then cooled, made alkaline with aqueous sodium hydroxide, and steam-distilled. The distillate was extracted with benzene, and the extract dried (K_2CO_3) and evaporated; it yielded *m*-cumidine (23·6 g.), b. p. 57·5°/0·4 mm., n_D^{25} 1·5440, which was dissolved in hydrochloric acid (25 ml.) and chilled in ice. The solid product was drained, recrystallised from benzene (800 ml.), and kept at reduced pressure over calcium chloride, sodium hydroxide, and paraffin wax. It (21·4 g.) yielded on a further recrystallisation m-*cumidine hydrochloride*, m. p. 158·5—159° (Found: Cl, 20·65. $C_9H_{14}ClN$ requires Cl, 20·65%).

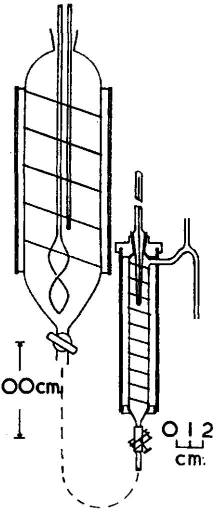


FIG. 1. *Apparatus for flow reaction.*

m-*Aminostyrene, and its Polymer and Copolymer with Styrene.*—The monomer was prepared by the method described earlier,[9] except that the preparation of *m*-nitrostyrene by heating small quantities of α-methyl-3-nitrobenzyl alcohol with phosphoric acid was replaced by the following more convenient flow-process. The apparatus is shown in Fig. 1; the mixing and the reaction vessel were lagged with asbestos wool, and the winding of each was connected to a Variac. The connection between the vessels was constricted by incorporation of 50 cm. of 2·5 mm.-bore glass tubing. The alcohol (25 g.) and orthophosphoric acid (*d* 1·74; 200 ml.) were heated with stirring at 58—60° in the mixing vessel, a homogeneous solution being obtained. This was then allowed to run through the reaction vessel at a rate controlled by the screw-clip. In this way, the *m*-nitrostyrene was removed from the heated zone soon after its formation, a process assisted by the fact that it separates as an oil which floats on phosphoric acid. The oil was removed and the lower layer recycled. Finally, the combined product was diluted with water (1 l.) and steam-distilled. The distillate was extracted with benzene, and the extract was washed with water and dried (K_2CO_3); t-butylcatechol (0·02 g.) was added. The alcohol (174 g.) was dehydrated in 25-g. portions as above; the flow-rate was 5 ml./min., and the reaction temperature 135°; the benzene extracts yielded *m*-nitrostyrene (54 g.), b. p. 80·5—83°/1 mm., n_D^{25} 1·5805.

In the isolation[9] of *m*-aminostyrene, quinol was replaced by t-butylcatechol as stabiliser. The amine had b. p. 64—66°/0·5 mm., n_D^{25} 1·6062; Schotten–Baumann benzoylation and recrystallisation from benzene–ligroin yielded *m*-benzamidostyrene, m. p. 93—93·5° (Komppa[10] records m. p. 90—91°).

Styrene (quinol-inhibited) was thrice washed with 2N-sodium hydroxide and with water, dried (Na_2SO_4), and distilled in oxygen-free nitrogen; it had b. p. 64·5°/49 mm., n_D^{25} 1·5441.

αα′-Azoisobutyronitrile [recrystallised from ether; m. p. 102·5—103·5°; (i) 0·031, (ii) 0·056 g.] was dissolved in *m*-aminostyrene [(i) 14·99, (ii) 14·01 g.] which was then sealed under nitrogen in a Pyrex tube and kept at 78—80° for (i) 4, (ii) 5 hr. The tube was chilled in solid carbon dioxide which facilitated the subsequent breaking-away of the glass from the polymer, a clear, pale yellow rubbery solid. It was dissolved, with stirring on a steam-bath, in dimethylformamide (75 ml.). The resultant clear viscous solution was added dropwise with high-speed stirring to water (600 ml.); the precipitate was collected on a Buchner funnel (without paper),

[9] Arcus and Schaffer, *J.*, 1958, 2428.
[10] Komppa, *Ber.*, 1893, **26**, 677.

washed with water (500 ml.) and methanol (200 ml.), and dried at reduced pressure over calcium chloride and paraffin wax. The polymer [(i) 6·51, (ii) 7·35 g.], also the copolymers below, were white and fibrous; they contained 1—2% of water, which was removed from specimens for analyses and viscosity determinations by heating to constant weight at 40°/1 mm. [Found: for polymer (i), N, 11·85; for polymer (ii), N, 11·65. Calc. for C_8H_9N: N, 11·75%].

The procedure above being followed, styrene, *m*-aminostyrene, and αα'-azoisobutyronitrile [(i) 21·66, 12·40, 0·067; (ii) 17·56, 10·05, 0·110 g. respectively] were allowed to react for (i) 28, (ii) 10 hr. The dimethylformamide solution (10 ml. per g.) was filtered from a small quantity of undissolved particles by passage through a pad of asbestos which was several times replaced. Precipitation yielded the copolymer [(i) 22·7, (ii) 16·2 g.] [Found, for copolymer (i): C, 88·1; H, 7·65; N, 4·2. Calc. for $C_8H_8 : C_8H_9N = 2{\cdot}00 : 1$; C, 88·05; H, 7·7; N, 4·3%].

The intrinsic viscosity, $[\eta]_c = (1/c)\ln(\eta_{\text{soln.}}/\eta_{\text{solv.}})$, where $c =$ g. of solute in 100 ml. of solution, was determined for the polymer and copolymer in solution in aniline at 24·8° and *c* 0·500. For polymer (i) and (ii) and copolymer (i) and (ii) there were found respectively $[\eta]_c$ 0·52, 0·43, 1·04, 0·45.

Rate-determination Procedure.—The method of preparation of the diazonium chloride solutions was conditioned by the solubility properties of the styrene–*m*-aminostyrene copolymer. This copolymer is insoluble in water and in methanol; on being heated with hydrochloric acid it yields the hydrochloride, which is insoluble in water but dissolves in methanol; the methanolic solution tolerates considerable dilution with water.

Equal volumes of water and redistilled methanol were mixed, and solutions of aniline hydrochloride and *m*-cumidine hydrochloride in this solvent were prepared such that each contained $14{\cdot}90 \times 10^{-4}$ mole per 150 ml.

Polymer (i) (0·015 mole) was dissolved by warming it with the exact equivalent of N-hydrochloric acid and methanol (40 ml.) for 30 min. Further methanol (710 ml.) and water (735 ml.) were added and the solution was filtered. Its concentration was determined by precipitation, from aliquot parts by aqueous sodium hydroxide, of the polyamine, which was collected, washed free from alkali, and dried at 110° to constant weight; the solution contained $15{\cdot}35 \times 10^{-4}$ mole/150 ml. A solution of polymer (ii), containing $15{\cdot}16 \times 10^{-4}$ mole/150 ml., was similarly prepared.

Copolymer (i) (0·030 mole) was treated with hydrochloric acid (100 ml.) and methanol (0·5 ml.; necessary to wet the copolymer), then heated for 3 hr. on a steam-bath. The mixture was diluted with water (600 ml.) and the copolymer hydrochloride filtered off and washed with water. It was at once dissolved in methanol (1500 ml.); water (1500 ml.) was then added. The resulting solution, which was clear and stable, contained $14{\cdot}90 \times 10^{-4}$ mole/150 ml. A solution of copolymer (ii), containing 15·04 mole/150 ml., was similarly prepared.

The aqueous-methanolic solution of the hydrochloride (150 ml.) was pipetted into the conical reaction flask, which contained a Polythene-covered magnetic stirrer. Hydrochloric acid (1·0 ml.) was added and the stirred solution was cooled in ice to <5°. Sodium nitrite (in 3% excess of the equivalent of the amine present) in water (5·0 ml.) was added, followed by water (25·0 ml.); stirring at <5° was continued for a further 2 hr., then stopped, and nitrogen passed through the solution for 30 min. The B14 joint comprising the neck of the flask was then connected to a two-way tap set to give access to the atmosphere; the reaction solution filled the flask up to the joint. The tap was then turned to connect the flask, through tubing of 2 mm. internal diameter, to the top of the nitrometer, which was filled with water saturated with nitrogen. Tubing and nitrometer were surrounded by water-jackets through which water from the thermostat bath was pumped. The flask was transferred from the ice-bath to the thermostat bath at 29·8° and the stirrer started. It had been found in control runs that the contents of the flask reach the temperature of the thermostat in 15 min., whence zero time and volume for measurement were taken at 20 min. after immersion of the flask in the thermostat bath. The final volume of nitrogen was noted when the reading had not changed for 2 hr.

Quadruplicate runs were carried out under the above conditions for each of the diazonium chlorides. In addition, duplicate runs were made with the diazonium chloride of copolymer (ii) at a higher acidity; the procedure was as above except that the addition of water was reduced from 25·0 to 16·0 ml., and 9·0 ml. of hydrochloric acid were added after the passage of nitrogen.

Products of Decomposition.—Polymeric. The precipitates from the rate-determination runs were collected, washed with water until the washings contained no chloride ion, and dried at 110°/1 atm. and then at 40°/1 mm. [Found: for the product from polymer (i): C, 78·75; H, 6·5; Cl, 3·15; N, 2·5; O, 8·75. For that from copolymer (i): C, 86·95; H, 7·3; Cl, 1·1; N, 0·9; O, 4·45%].

Benzenediazonium chloride. (*a*) Aniline hydrochloride (12·96 g.) was dissolved in methanol (75 ml.), water (6 ml.), and 2·00N-hydrochloric acid (100 ml.). The solution was cooled to 0—5° and to it was added sodium nitrite (7·11 g.) during 35 min. After a further 2 hr. at this temperature, the solution was kept at 30° for 48 hr. An oil had then separated. The whole was steam-distilled; the first part of the distillate, containing methanol, was further diluted with water; the distillates were extracted with ether, and the combined extracts subjected to a conventional separation of acidic and non-acidic products. There were obtained phenol (4·27 g.) (which yielded phenyl benzoate, m. p. 69°) and a mixture of anisole and chlorobenzene. The mixture was identified and its composition determined by comparison of the two peaks shown on its gas-liquid chromatogram with those for three mixtures of known quantities of authentic anisole and chlorobenzene. A 120 cm. column of 20% squalane on 100—120 mesh Celite-545 was used at 77°. There were found: anisole, 1·48 g.; chlorobenzene, 0·42 g.

(*b*) The procedure was as above except that the initial solvent was composed of 11·7N-hydrochloric acid (67 ml.), methanol (75 ml.), and water (39 ml.). There were obtained: phenol, 3·52 g.; anisole, 1·34 g.; chlorobenzene, 2·20 g.

RESULTS AND DISCUSSION

m-Cumidine was synthesised by the known route from cumene with certain modifications (see above). Polymerisation of *m*-aminostyrene is recorded by Dahlig[11] who heated the monomer with benzoyl peroxide, alone and in dioxan, and obtained a brown syrup. It is inferred that the initiator is spent in oxidising amino-groups. Initiation with αα′-azoisobutyronitrile at 79° was satisfactory; two specimens of poly-(*m*-aminostyrene) and two of 2 : 1 styrene–*m*-aminostyrene copolymer were prepared, one of each pair being formed with 0·2% and one with 0·4% of initiator. The polymers and copolymers, on dissolution in dimethylformamide and precipitation with water, were obtained as fibrous white solids.

A ruling consideration in the present work has been to establish conditions under which all the diazonium chlorides can be obtained completely in solution. The copolymer is the least tractable of the four amines. The procedure described in the Experimental part yields the diazonium chloride of the copolymer in 0·0083N-solution in aqueous methanol having the volumes of the components in ratio 59 : 41. The composition of this solution has defined the conditions under which the rates of diazonium decomposition have been measured, each of the other diazonium chlorides being prepared in similar solution.

Order of Decompositions.—Representative examples of runs for benzene- and cumene-*m*-diazonium chloride, and the diazonium chlorides of poly-(*m*-aminostyrene) and styrene–*m*-aminostyrene copolymer are shown in Fig. 2. First-order constants (*k*) are given in the Table.

The logarithmic plots for the decomposition of benzenediazonium chloride show substantial linearity. Pray[12] has determined first-order constants for this reaction in a wide range of methanol–water mixtures at 30°; interpolation in his results yields $k = 1·17 \times 10^{-4}$ sec.$^{-1}$ for the solvent composition used in the present experiments.

To 70% of the measured decomposition, the plots for cumene-*m*-diazonium chloride are substantially linear.

For the polymer, as reaction proceeds, the logarithmic plots become concave towards the abcissa; however, up to 70% reaction the departure from linearity is not great. After about 80 min. from zero time precipitation of the polymer began in each run; this caused no sharp change in the plots, occurred after 75% decomposition, and therefore lay beyond the region for which the constants have been deduced.

For the copolymers, precipitation commenced after about 8 min. For most of the run, therefore, the polymer was present partly as a swollen solid. Nevertheless, the

---

[11] Dahlig, *Prace Placówek Navk-Badawcz Ministerstwa Przemyslo Chem.*, 1952, **1**, 29.

[12] Pray, *J. Phys. Chem.*, 1926, **30**, 1477.

departure from linearity is small. The onset of precipitation is parallelled by a displacement in the logarithmic plot of the run (Fig. 2); the pre-precipitation sections are substantially linear, yielding first-order constants which, however, are not as accurate as the main constants owing to the short time- and volume-ranges; the values for copolymer (i) average 3·0 and for copolymer (ii) $3{\cdot}4 \times 10^{-4}$ sec.$^{-1}$.

With the diazonium chloride derived from copolymer (ii), two runs were carried out at a higher acidity (excess of hydrochloric acid 0·64N instead of 0·056N). Precipitation began as soon as the further quantity of acid was added, *i.e.*, 20 min. before zero time; however, the runs gave logarithmic plots of good linearity and the rate constants show an increase of 10%; this is considered small in relation to the change in acidity and precipitation.

First-order decomposition at 29·8° (k; 10^{-4} sec.$^{-1}$)

Diazonium chloride derived from	Individual runs					Average
Aniline	1·15	1·12	1·14	1·16	1·12	1·14
m-Cumidine	6·96	7·30	7·07	7·25		7·15
Poly-(*m*-aminostyrene) (i)	3·39	3·49	3·45	3·64		3·49
,, ,, (ii)	3·63	3·36	3·47	3·34		3·45
2 : 1 Styrene–*m*-aminostyrene copolymer (i)	3·09	3·19	3·02	3·02		3·08
,, ,, ,, (ii)	3·17	3·03	3·27	2·99		3·12
,, ,, ,, (ii) *	3·34	3·45				3·40

* At higher acidity.

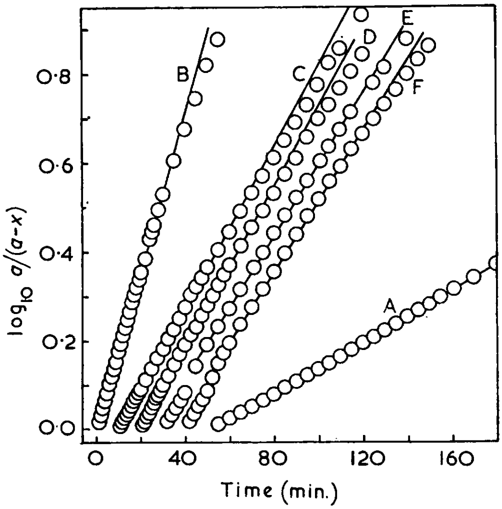


FIG. 2. *Rates of decomposition of diazonium chlorides derived from*: A, *aniline*; B, m-*cumidine*; C, D, *poly*-(m-*aminostyrene*) (i) *and* (ii); E, F, 2 : 1 *styrene*–m-*aminostyrene copolymer* (i) *and* (ii). *The time-origin has been displaced by* 10 *min. for each successive compound. Ordinate values of* 0·52 *and* 0·70 *correspond to* 70% *and* 80% *of the total observed reaction.*

Products.—The precipitates from the decomposition of the polymeric and copolymeric diazonium salts, after being washed and dried, were dark red solids which when finely ground formed orange powders. No solvent was found for these materials; they were not analysed for functional groups, as no reliance could be placed on the results for insoluble and possibly cross-linked solids; elemental analyses show the greater part of the nitrogen to have been replaced by oxy-groups, some nitrogen remaining, and some chlorine being present, but the number of types of structural unit which may have been formed is too great to permit deduction of the total structure.

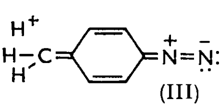
However, the course of the reaction for benzenediazonium chloride in the aqueous methanol used in the kinetic runs has been ascertained. It was necessary to increase the concentration of diazonium salt sixty-fold in order to obtain quantities of product convenient for isolation and separation, so the exact conditions of the kinetic runs could not be employed. Accordingly, two sets of acidic conditions were used: (*a*) with the same concentration of excess of hydrochloric acid, and hence less than the molar ratio of acid to diazonium chloride of the kinetic runs; (*b*) with the molar ratio of excess of hydrochloric acid to diazonium chloride of these runs, and hence a higher concentration of acid than obtained therein. There were isolated:

Conditions	PhOH *	PhOMe *	PhOMe/PhOH	PhCl *
(*a*)	45	14	0·31	4
(*b*)	37	12	0·32	20

* Yield as moles per 100 moles of PhN_2Cl. The presence of methanol at extraction and evaporation stages militates against complete isolation of phenol.

Phenol is the main product, and anisole bears an approximately constant ratio thereto; the yield of chlorobenzene is increased by the higher hydrochloric acid concentration of conditions (*b*). Thus, as a result of diazonium decomposition, the entry of hydroxyl, methoxyl, and chlorine into the polymer and copolymer is to be expected; from the colour and nitrogen content of the products, the presence of azo-linkages is probable, and, by analogy with the production of 4-hydroxybiphenyl in the reaction of benzenediazonium chloride with phenol,[13] the formation of hydroxybiphenyl units within or between macromolecules is possible.

Relationship of Rate-constants and Structure.—The insertion of electron-attracting substituents in the benzenediazonium cation reduces the rate of decomposition, in accordance with equation (1).[14] With respect to electron-releasing substituents, the position is complex, it being notable that *p*-alkyl substituents reduce the rate of decomposition: this stabilisation of the diazonium ion has been ascribed to hyperconjugation, form (III) contributing to the constitution of the toluene-*p*-diazonium cation and strengthening the C–N bond.[14,3] The question whether a combination of conjugative and inductive effects is adequate to account generally for the observed rates of decomposition of alkylbenzenediazonium cations has been critically discussed by Lewis and Miller.[3] However, for *m*-alkylbenzenediazonium cations, the following data are recorded:


(III)

m-Alkyl substituent	None	Me	Et	Bu^t
k (10^{-4} sec.$^{-1}$) at 29·9—30·0°	0·992	3·92	6·93	14·1
Initial solvent	Water [1]	0·1N-Hydrochloric acid [3]		

For *meta*-substitution, in which hyperconjugation is presumably ineffective, it is tenable that the relative rates are accounted for by the progressive increase in inductive electron-release on passage from hydrogen to the methyl, ethyl, and t-butyl groups, and this has been assumed.

With respect to the present results for reaction in aqueous methanol, it is seen (Table) that the substitution of a *m*-isopropyl group in benzenediazonium chloride increases the rate of decomposition six-fold. The rate constants for the diazonium chlorides of poly-(*m*-aminostyrene) and the 2 : 1 styrene–*m*-aminostyrene copolymer are intermediate between those for benzene- and cumene-*m*-diazonium chloride. The primary macromolecular structure which forms the environment of the phenyldiazonium group is shown in (II): for the polymer, X and Y are initially other *m*-benzenediazonium groups and subsequently the derived groups the nature of which is discussed above; for the copolymer X and Y may be as just described, but generally must be phenyl groups. In every instance (though to different extents) inductive electron-withdrawal from the structure in the square brackets is probable, whence it is concluded that the electron-release from the main chain to the benzenediazonium group is some fraction of that from an isopropyl group, in accord with the relation between the rate constants described above.

The polymeric diazonium cation differs from the copolymeric cation in the following respects: (*a*) the benzenediazonium groups are adjacent to a much greater extent in the

---

[13] Hirsch, *Ber.*, 1890, **23**, 3705.

[14] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 294.

polymer than in the copolymer; (*b*) the charge on a given chain length of the polymer is thrice that on the same length of copolymer; (*c*) this might be expected to lead by repulsion to a more extended conformation of the polymer than the copolymer; (*d*) during reaction, precipitation of the polymer occurs later than that of the copolymer. The decomposition rate for the polymer is 11% greater than that for the copolymer. It is not possible to relate factors *a, b, c,* and *d* with certainty to this relatively small difference, except to infer from it and the results as a whole that these factors exert only a minor influence on the course of diazonium decomposition.

It is concluded, with respect to the population of *m*-benzenediazonium groups attached to polyvinyl main chains, that: (i) decomposition is unimolecular; (ii) electron-release from the chain to the side-groups influences the rate in a manner accountable by reference to appropriate small molecules; (iii) specifically macromolecular reactivity-factors have little influence on this reaction.

We thank Dr. T. J. Howard for the gas–liquid chromatography, and the Chemical Society and Imperial Chemical Industries Limited for aid from grants.

BATTERSEA COLLEGE OF TECHNOLOGY, LONDON, S.W.11. [*Received, March 14th,* 1961.]