993. *Radiation-induced Decomposition of Ion-exchange Resins. Part I. Anion-exchange Resins.*

By G. R. Hall and M. Streat.

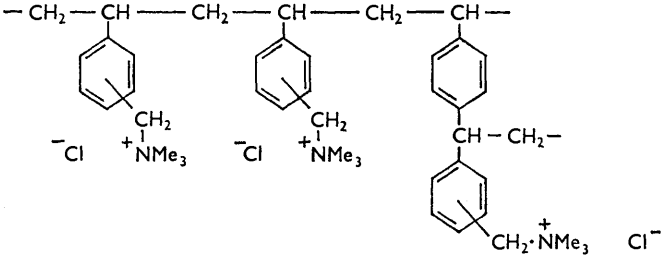
Aqueous slurries of the anion-exchange resin Deacidite FF in the hydroxide form have been irradiated with ^{60}Co γ-rays. Severe chemical decomposition was observed at doses of up to 500 Mrad, chiefly by the destruction of strong-base functional groups resulting in the release of water-soluble aliphatic amines. Analytical techniques for the estimation of individual amines in mixtures are described, and quantitative yields of tertiary, secondary, and primary amines, and ammonia are reported. Traces of formaldehyde have been detected, but peroxides and nitrites have been found to be absent in the aqueous solutions associated with the irradiated resin. Total anion-exchange capacity does not fall as rapidly as strong-base quaternary capacity. It has been shown that an increase in weak-base capacity is due to some conversion of quaternary groups into weak-base amine groups, caused by irradiation. Decomposition of the quaternary functional groups appears to proceed by a simple Hofmann degradation. Possible mechanisms for the production of other products are discussed.

The radiation-induced decomposition of ion-exchange resins has been reported in a number of papers,[1] but such studies have been mainly qualitative and confined to the observation of capacity changes. The strong-base anion-exchangers, *e.g.*, polystyrene-based resins with quaternary ammonium functional groups, have been shown to lose exchange capacity at high doses, accompanied by the release of basic products thought to be amines and ammonia. Smith and Groh [1d] examined leach solutions containing these products by infrared techniques, but the spectra were too complicated for analysis.

In this work, methods have been devised for the quantitative analysis of basic products, and their yields have been measured for resin samples irradiated in the hydroxide form. Measurements have also been made of the changes in exchange capacity, and these have been correlated with the yields of basic products to give a quantitative picture of the overall resin decomposition.

Experimental

The anion-exchange resin Deacidite FF (The Permutit Company Limited) was supplied in the chloride form, 7—9% cross-linked and screened to 100—200 mesh in the fully swollen state. The structure of the resin is:



Samples were prepared for irradiation by washing with distilled water, with warm methanol to remove organic impurities, and then leaching with N-sodium hydroxide to prepare the hydroxide form. Replacement of chloride by hydroxide ions is slow. By passing two column-volumes of 1N-sodium hydroxide, under conditions recommended by the manufacturer, a

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[1] (*a*) Higgins, Radiation Damage to Ion Exchange Resins, U.S. Atomic Energy Commission Report ORNL–1325, 1953; (*b*) Fisher, Effect of Gamma Radiation on Ion Exchange Resins, U.S.A.E.C. Report RMO–2528, 1954; (*c*) Wedemeyer, Ph.D. Thesis, Vanderbilt, 1953; (*d*) Smith and Groh, The Effect of Gamma Radiation on Ion Exchange Resins, U.S.A.E.C. Report DP–549, 1961.

strong-base capacity of 1·4—1·8 mequiv./g., with respect to hydroxide ion, was obtained. Resin samples used in this work had a hydroxide capacity of 2·3 mequiv./g., whereas the total strong-base capacity, with respect to chloride ion, was measured as 4·0 mequiv./g., and weak-base capacity as 0·2 mequiv./g. It was subsequently found that continuous leaching with N-sodium hydroxide for several days led to complete conversion.

Samples (1—2 g.) of a water slurry of the resin were irradiated in stoppered (ungreased) test-tubes, placed 3 cm. from a kc ^{60}Co source.[2] Most irradiations were at a constant dose-rate of $6\cdot1 \times 10^5$ rads/hr. Dose-rates were measured by the Fricke dosimeter, using values for $G(\mathrm{Fe}^{2+}$ oxidised) as 15·50 at 20° in 0·1N-sulphuric acid.[3]

After irradiation, resin samples were washed with water until free from decomposition products, the washings being collected for further analysis. The resin samples were treated for capacity measurement and dried in the sulphate form at 100° for 24 hr. before weighing. Capacities reported here refer to mequiv. of exchange capacity per gram of dry resin weighed in the sulphate form.

Measurement of Exchange Capacity.—Strong- and weak-base capacities were measured by a method similar to that described by Fisher and Kunin.[4] Those quaternary groups in the hydroxide form were converted into the chloride form by passing an excess of 4% sodium chloride through a bed of the appropriate resin. The effluent was collected and titrated against 0·1N-hydrochloric acid to give the strong-base hydroxide capacity. The resin was then washed with 4% hydrochloric acid to ensure that weak-base groups were converted into the hydrochloride form. Excess of chloride ions were removed by washing with methanol; this avoids hydrolysis of the hydrochloride on the weak-base groups. Subsequent leaching with 0·15M-ammonium hydroxide, hydrolysed these hydrochloride groups and released hydrochloric acid, the strong-base groups remaining unaffected. The concentration of chloride ion in the effluent was therefore a measure of the weak-base capacity. By then leaching the resin with 4% sodium sulphate solution, the remaining chloride groups attached to the strong-base functional groups were replaced by sulphate ions. The strong-base capacity was therefore obtained by measuring the chloride-ion concentration in this leach solution. Chloride ion was estimated by Volhard's procedure.

The possible uptake of carbon dioxide from the atmosphere, leading to conversion of hydroxide into carbonate on the strong-base groups, was considered. To check this, samples of the hydroxide form of the resin in aqueous slurry were set aside in contact with the atmosphere for 4 weeks, after which the measured carbonate capacity was not greater than 2% of the total strong-base capacity.

Kjeldahl Estimation of Total Nitrogen in Aqueous Leach Solutions Containing Basic Products.—The leach solution was digested with concentrated sulphuric acid and a selenium catalyst to break down nitrogenous products. The solution was made alkaline and steam-distilled into acid, the excess of acid being titrated directly against sodium carbonate solution to give the total amount of nitrogen released.

Estimation of Tertiary Amine.—The method used was based on the procedure developed by Dyer,[5] who modified the picrate method used by Richter, Lee, and Hill [6] for the determination of dimethylamine. Dyer's method is based on the measurement of the yellow colour of the amine picrate in an organic solvent; it was developed here to determine trimethylamine quantitatively in the presence of comparable amounts of dimethylamine and methylamine, by taking into account the contribution of the latter two amines to the absorption at 410 mμ.

The procedure was to dilute a suitable quantity of the amine sample to 4 ml. and then add 1 ml. of a soln. of 37% formaldehyde which had been shaken with magnesium carbonate. To this was added toluene (10 ml.) and 50% potassium carbonate soln. (3 ml.), the mixture shaken, and the toluene layer dried ($\mathrm{Na_2SO_4}$). Picric acid (5 ml.) (0·02% in dry toluene) was added to the dried toluene layer (5 ml.) and the yellow colour measured at 410 mμ (ε 180) against a reagent blank. It has been shown [7] that the sensitivity of the method to tertiary, secondary, and primary amines is in the ratio 20 : 4 : 1. A sufficiently accurate estimation of tertiary amine

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[2] Hall and Streat, *J. Imp. Coll. (London) Chem. Eng. Soc.*, 1962, **13**, 84.
[3] Haybittle, Saunders, and Swallow, *J. Chem. Phys.*, 1956, **25**, 1213.
[4] Fisher and Kunin, *Analyt. Chem.*, 1955, **27**, 1191.
[5] Dyer, *J. Fisheries Research Board Canad.*, 1950, **7**, 576.
[6] Richter, Lee, and Hill, *Biochem. J.*, 1941, **35**, 1225.
[7] Streat, Ph.D. Thesis, London, 1961.

can be made (±2%) by correcting for the contribution of the secondary amine to the optical density at 410 mμ, the absorption of primary amine usually being small enough to be neglected.

Estimation of Secondary Amine.—A rapid and reproducible method developed by Stanley, Baun, and Gove [8] was used for the estimation of secondary amine. The amine reacted with carbon disulphide and ammonia to form the dialkylthiocarbamate, and the colour of a benzene extract of the copper complex was measured at 434 mμ.

To a sample (10 ml.) was added a reagent solution (1 ml.) containing ammonium acetate (20 g.) and copper sulphate (0·2 g.) in water (30 ml.) to which had further been added sodium hydroxide (10 g.) in water (25 ml.) and concentrated ammonia (20 ml.), the whole having been diluted to 100 ml. with water. A 5% solution of carbon disulphide in benzene (10 ml.) was added to the mixture of sample and reagent solution and this was then heated to 43—48° and shaken vigorously before 30% acetic acid solution (1 ml.) was added. The organic layer was separated, centrifuged, and measured against a reagent blank at 434 mμ (ε 600). Other amines did not interfere when present in similar concentrations. The method was reproducible to ±2%, under carefully controlled conditions.

Estimation of Primary Amine.—The diazonium salt, formed when *p*-nitroaniline reacts with acidified sodium nitrite, will couple with primary amines and this reaction can be used for quantitative estimation of the amine.[9]

A reagent solution was prepared by dissolving *p*-nitroaniline (0·5 g.) in N-hydrochloric acid (100 ml.) and cooling to 0°. 3% Sodium nitrite solution (10 ml.) previously cooled in ice, was added 30 min. before required and the resultant solution stored in the dark. To a sample (1 ml.) was added buffer (10 ml.) (pH 9·4) and the solution cooled in ice. Reagent (1 ml.) was added, followed, after 20 min., by 10% sodium hydroxide (1 ml.). Tertiary and secondary amines did not interfere and ammonia did not interfere at concentrations less than that of the primary amine. The red colour produced was measured at 510 mμ (ε 1500) after 24 hr. The method was reproducible to within 10%, providing a carefully controlled procedure was used.

Estimation of Ammonia.—Ammonia can be estimated in the presence of amines as the blue-coloured complex formed with a phenol–sodium hypochlorite reagent.[10] Although this method is suitable in the presence of tertiary and secondary amines, large amounts of primary amines interfere. Bolleter, Bushman, and Tidwell [11] have modified this method by using freshly prepared chlorine water in place of sodium hypochlorite.

The ammonia sample (1 ml.) was transferred to a 50 ml. flask, and saturated boric acid soln. (25 ml.) was added, followed by saturated chlorine water (5 ml.) and 8% phenol solution (5 ml.). The mixture was heated on a steam-bath for 3 min., and then cooled, 3M-sodium hydroxide soln. (5 ml.) was added, and the solution made up to 50 ml. The blue colour, which developed after 5 min., was measured at 625 mμ (ε 100) against a reagent blank. Both methods were tested, the latter being some 30 times less sensitive to primary amines than to ammonia.

Estimation of Formaldehyde.—The violet colour formed when formaldehyde reacts with chromotropic acid was measured at 580 mμ. The method was reproducible to ±3%.[12]

RESULTS AND DISCUSSION

The effect of γ-radiation on the anion-exchange capacity of Deacidite FF resin is shown in Fig. 1. There is a marked decrease in the total capacity (strong + weak base) over a range of 0—500 Mrad. The strong-base hydroxide capacity has decreased almost to zero in this range, although the overall strong-base capacity, measured with respect to chloride ions, has not decreased to the same extent, *i.e.*, the strong-base functional groups have not been completely destroyed. This difference is due to the initial functional groups' not being completely in the hydroxide form at the start of the irradiation. Resins in the salt form are generally more resistant to irradiation than those in the hydroxide

[8] Stanley, Baun, and Gove, *Analyt. Chem.*, 1951, **23**, 1779.
[9] Persez and Poirier, *Bull. Soc. chim. France*, 1953, 745.
[10] Crowther and Large, *Analyst*, 1956, **8**, 64.
[11] Bolleter, Bushman, and Tidwell, *Analyt. Chem.*, 1961, **33**, 593.
[12] Salterfield, Wilson, and Leclair, *Analyt. Chem.*, 1954, **26**, 1792.

form. This has been found in measurements of the chloride[13] and nitrate forms.[14] The net effect, however, is seen to be a decrease in strong-base capacity.

A significant and steady increase in the weak-base capacity, resulting from the replacement of quaternary functional groups by tertiary groups, is observed. A similar result was reported by Smith and Groh[1d] in their irradiation of Dowex-1 resin, which has an almost identical structure. The overall increase in weak-base capacity is, however, only small compared to the net loss in strong-base capacity.

The quantitative yields of basic products produced by irradiation are shown in Fig. 2, and *G*-values for their formation are given in Table 1. This shows a predominance of tertiary amine in the aqueous solutions associated with the irradiated resin, with yields of secondary and primary amine and ammonia increasing as the irradiation proceeds. The yield for the formation of ammonia is only small up to 100 Mrad, but becomes constant at $G = 1{\cdot}3$ above *ca.* 150 Mrad. It would seem that ammonia is the final decomposition product; we have tested for hydroxylamines and oxides of nitrogen but have not found them in significant yields, *i.e.*, greater than 10^{-3} mequiv./g.

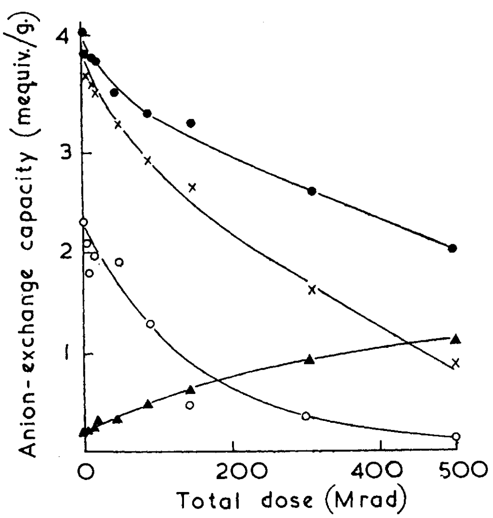

FIG. 1. Anion-exchange capacity as a function of total dose.

●, Total capacity; ×, strong-base capacity; ○, hydroxide capacity; ▲, weak-base capacity.

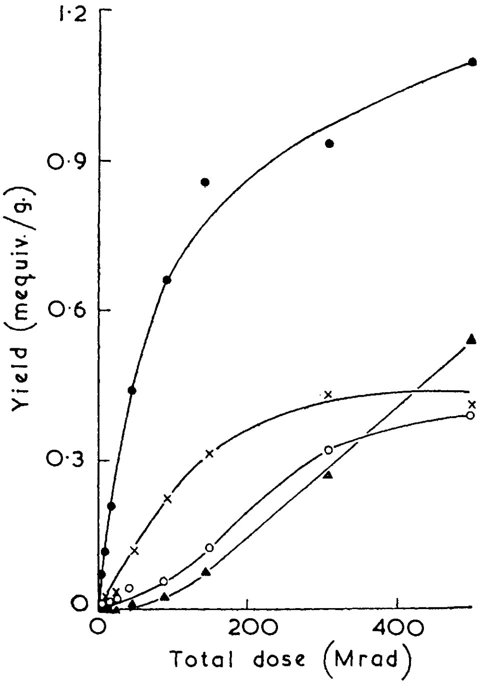

FIG. 2. Yield of basic products as a function of total dose.

●, Trimethylamine; ×, dimethylamine; ○, methylamine; ▲, ammonia.

Fig. 3 has been plotted to show the relation between the loss in total capacity and the basic products released. Taking into account experimental errors, and a weight-loss which is not expected to be greater than 10% for loss of functional groups at 500 Mrad, the graph shows that practically all the loss in capacity can be accounted for by the production of the basic products, *e.g.*, tertiary, secondary, and primary amines, and

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[13] Shigematsu and Oshio, *Bull. Inst. Chem. Res., Kyoto Univ.*, 1959, **37**, 349.

[14] Hall and Natarajan, to be published.

ammonia. The mean deviation of the experimental from the theoretical curve in the range 0—500 Mrad is 12%.

TABLE 1.

Measured *G*-values for formation of basic products.

Dose (Mrad)	Tertiary amine	Secondary amine	Primary amine	Ammonia
0	14·23	3·09	0·48	0
50	5·78	2·29	0·77	0
100	2·68	1·73	1·06	0·77
150	1·56	1·16	1·16	1·31
200	1·05	0·77	1·35	1·31
300	0·78	0·39	0·77	1·31
400	0·58	0·19	0·58	1·31
500	0·47	0·09	0·19	1·31

G-value = No. of molecules of product formed/100 ev radiation energy absorbed in the system.

The effect of dose-rate has been investigated at two values; the results are given in Table 2.

The loss of strong-base capacity follows a simple unimolecular rate law. This is analogous with measurements reported by Baumann[15] who found the thermal decomposition of the hydroxide form of a similar resin also followed a first-order rate law. Resin samples in the hydroxide form have been heated to 100° in aqueous slurry during this work, and found to yield only tertiary amine as a main product.[16] Secondary and primary amines and ammonia were not detected.

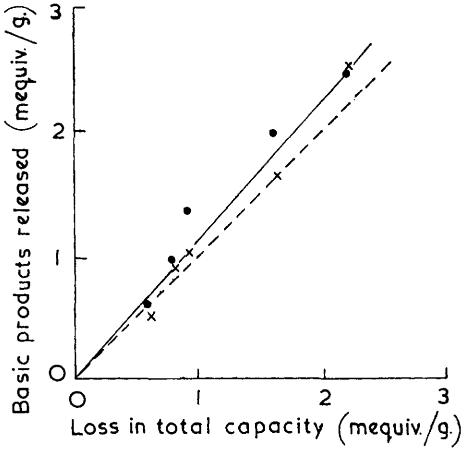

FIG. 3. Basic products released plotted against loss in total capacity on irradiation.

●, Total amine and ammonia by colorimetric analysis; ×, total volatile base by Kjeldahl estimation; – – – – theoretical line at 45°.

TABLE 2.

Effect of dose-rate on strong- and weak-base capacity and on yield of basic products.

Dose-rate (Mrad/hr.)	Total dose (Mrad)	Capacity (mequiv./g.)		Basic products (mequiv./g.)				
				Amines				
		Strong-base	Weak-base	Tertiary	Secondary	Primary	Ammonia	Total
0·61	55·0	3·11	0·42	0·47	0·11	0·04	0·01	4·16
0·18	65·0	2·94	0·45	0·51	0·13	0·04	0·01	4·08
0	—	3·80	0·22	—	—	—	—	4·02

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[15] Baumann, *J. Chem. and Eng. Data*, 1960, **5**, 376.

[16] Hall and Streat, to be published.

The apparent lack of dose-rate effects in the resin irradiations, over the limited range studied, seems to rule out appreciable contributions from chain mechanisms. Further work is being carried out to obtain a more complete understanding of the reactions involved, by irradiating resin samples throughout in the presence and total absence of oxygen and water.[14] The present work, however, indicates that a simple Hofmann degradation type of reaction, initiated by a direct absorption of radiation energy by the resin particles, best fits the results obtained. This is analogous to results obtained with resins heated in the hydroxide form, where the following simple reactions appear to take place: [15,16]

$$\mathrm{R{\cdot}CH_2{\cdot}NMe_3^+\,OH^-} \longrightarrow \mathrm{R{\cdot}CH_2{\cdot}OH + NMe_3} \tag{1}$$

$$\mathrm{R{\cdot}CH_2{\cdot}NMe_3^+\,OH^-} \longrightarrow \mathrm{R{\cdot}CH_2{\cdot}NMe_2 + MeOH} \tag{2}$$

These reactions explain the loss of quaternary functional groups with the production of tertiary amines and an increase in weak-base groups. However, it is necessary to postulate mechanisms for the formation of secondary amines, primary amines, and ammonia.

Secondary amines can be formed as follows: (*a*) directly from the resin, owing to the initial presence of a small number of weak-base groups; (*b*) by decomposition of weak-base groups formed from the original quaternary group by reaction (2). The following reaction is suggested:

$$\mathrm{R{\cdot}CH_2{\cdot}NMe_2 + H_2O} \longrightarrow \mathrm{R{\cdot}CH_2{\cdot}OH + Me_2NH} \tag{3}$$

(*c*) directly from the quaternary groups initially present. A reasonable reaction mechanism, analogous to that suggested for the radiolysis of amino-acids,[17] is that involving the formation of an intermediate imine:

$$\mathrm{R{\cdot}CH_2{\cdot}NMe_3^+\,OH^-} \longrightarrow \mathrm{R{\cdot}CH{:}NMe_2^+\,OH^- + CH_4} \tag{4}$$

$$\mathrm{R{\cdot}CH{:}NMe_2^+\,OH^- + H_2O} \longrightarrow \mathrm{R{\cdot}CHO + Me_2NH + H_2O} \tag{5}$$

A similar mechanism also explains the direct formation of primary amine and ammonia from weak-base groups produced on the resin as irradiation proceeds and by decomposition of aliphatic amines released in solution, *e.g.*,

$$\mathrm{Me_3N} \longrightarrow \mathrm{MeN{:}CH_2 + CH_4};\ \mathrm{MeN{:}CH_2 + H_2O} \longrightarrow \mathrm{MeNH_2 + CH_2O} \tag{6}$$

$$\mathrm{Me_2NH} \longrightarrow \mathrm{CH_2{:}NH + CH_4};\ \mathrm{CH_2{:}NH + H_2O} \longrightarrow \mathrm{NH_3 + CH_2O} \tag{7}$$

Removal of molecular hydrogen can also result in the destruction of aliphatic amine to produce ammonia:

$$\mathrm{Me_2NH} \xrightarrow{(-2\mathrm{H})} \mathrm{CH_2{:}NMe};\ \mathrm{CH_2{:}NMe + H_2O} \longrightarrow \mathrm{MeNH_2 + CH_2O} \tag{8}$$

$$\mathrm{MeNH_2} \xrightarrow{(-2\mathrm{H})} \mathrm{CH_2{:}NH};\ \mathrm{CH_2{:}NH + H_2O} \longrightarrow \mathrm{NH_3 + CH_2O} \tag{9}$$

All these reactions can lead to a final product of ammonia which is consistent with the experimental results and, furthermore, to yields of formaldehyde. Formaldehyde can, however, react with the aliphatic amines themselves, *e.g.*,

$$\mathrm{MeNH_2 + CH_2O} \longrightarrow \mathrm{MeNH{\cdot}CH_2{\cdot}OH} \tag{10}$$

and this could explain why only trace yields of formaldehyde were found.

Preliminary irradiations have been carried out with a model compound, $\mathrm{PhCH_2{\cdot}NMe_3^+\,OH^-}$ dissolved in water, in order to examine the reaction mechanisms of quaternary ammonium compounds more closely. Whereas it is difficult to characterise the grouping remaining on the polystyrene network after the irradiation of a resin sample, because of the inherent chemical stability of the polymer, this problem can be simplified by analysis of the products formed by irradiation of a model compound, in particular a

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[17] Swallow, " Radiation Chemistry of Organic Compounds," Pergamon Press, Oxford, 1961.

characterisation of the final form of the grouping attached to the phenyl radical. Qualitative measurements have so far shown that the primary products appear to be benzaldehyde and tertiary amine.[7] Secondary amine, primary amine, and ammonia are also present at doses of up to 1 Mrad. It is not clear at present that benzaldehyde is the only product formed from the benzene ring.

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DEPARTMENT OF CHEMICAL ENGINEERING AND CHEMICAL TECHNOLOGY,
NUCLEAR TECHNOLOGY LABORATORY,
IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON S.W.7.

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