

## NOTE

*The  $\gamma$ -Radiolysis of Zeocarb 225 Cation-Exchange Resins*

## Synopsis

Irradiation of Zeocarb 225 cation-exchange resin leads to a loss of exchange capacity and the formation of  $\text{SO}_4^{2-}$  ions.  $G(\text{SO}_4^{2-})$  is dependent upon the relative amount of water associated with the resin and may be reduced by the addition of scavengers, reactive towards hydroxyl radicals. The results suggest that both direct and indirect radiolyses are able to bring about desulphonation and that hydroxyl radicals are responsible for the indirect radiolysis.

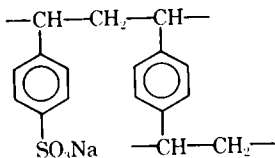
## INTRODUCTION

Capacity loss in irradiated sulfonic acid cation-exchange resins proceeds largely by the loss of sulfonic acid groups. Some workers appear to regard this effect as being mostly due to the direct radiolysis of the resin,<sup>1,2</sup> whereas others have discussed the degradation in terms of attack by water radiolysis products.<sup>3,4</sup> It seems, however, more reasonable that the damage can be brought about by both mechanisms, and this point has been made by Egorov and Novikov.<sup>5</sup>

In this paper we have attempted to assess the relative extents of direct and indirect radiolysis by studying the effect of varying water content upon the rate of formation of  $\text{SO}_4^{2-}$  ions, which appear to be the major products of desulfonation. A qualitative identification of the species responsible for indirect damage has been sought by the use of scavengers. A similar approach proved useful in studies of the deamination of quaternary ammonium anion-exchange resins.<sup>6</sup>

## EXPERIMENTAL

The irradiations were carried out on Zeocarb 225, a polystyrene-based sulfonic acid cation exchange resin, 8% crosslinked. The structure can be represented by:



The sodium form of the resin was used in all the experiments reported here. The resin was washed successively with demineralized water, warm methanol, 4% sodium chloride, and finally demineralized water until no further chloride ions could be detected. After this treatment the resin samples were dried at 60°C and stored in a desiccator.

Samples of the stock resin, 1 g each, were further dried to constant weight at 105°C (about 24 hr). Completely slurred resins were obtained by adding water to the dry resins until the solid was just covered. This gave a resin-to-water ratio of 1:2. Other ratios were obtained by equilibration with water vapor or by the dropwise addition of water and subsequent equilibration in a closed vessel. All the water contents were established by weighing, heating to 105°C, and reweighing.

Irradiations were carried out in stoppered borosilicate glass tubes at dose rates in the range  $1.7 \times 10^{17}$  to  $1.4 \times 10^{18}$  eV/g per min (maximum dose,  $7 \times 10^{21}$  eV/g). The dose rates were measured by the Fricke dosimeter and by taking  $G(\text{Fe}^{3+}) = 15.5$ .

The tubes containing the resin samples were purged with oxygen-free nitrogen before irradiation. Estimation of the  $\text{SO}_4^{2-}$  yield was carried out by washing the irradiated resin with water and collecting the combined washings for analysis by the method of Belcher and Kolthoff.<sup>7</sup>

## RESULTS AND DISCUSSION

### Effect of Varying the Proportion of Water in the Resin

Table I shows the variation in  $G(\text{SO}_4^{2-})$  when samples of Zeocarb 225 mixed with various proportions of water were irradiated. It is seen that the addition of water to the dry resin results in an initial rise in  $G(\text{SO}_4^{2-})$  but that at higher water contents  $G(\text{SO}_4^{2-})$  decreases once more.

TABLE I  
 $\gamma$ -Irradiation of Mixtures of Zeocarb 225 and Water:  
Effect of Varying Water Content on  $G(\text{SO}_4^{2-})$

$G(\text{SO}_4^{2-})$	Weight fraction of Water	Fraction of energy absorbed by water
0.22	dry	—
0.97	0.18	0.19
1.11	0.41	0.43
1.04	0.46	0.48
0.53	0.66	0.69

The  $G$ -values in all cases have been calculated on the basis of the total energy absorbed in the system (resin + water), assuming that the relative energy absorption coefficients of the fully sulfonated resin is 0.92 of that for the Fricke dosimeter.<sup>8</sup>

It is useful to consider the results in three regions of water content: (a) the region dry resin—water fraction 0.2; (b) water fraction 0.2–0.4; and (c) water fraction  $>0.4$ .

The  $G(\text{SO}_4^{2-})$  value for dry resin is very low and is probably not typical of the production of  $\text{SO}_4^{2-}$  ions by direct radiolysis of the resin in systems containing water. That is, it is probable that water is necessary if the  $-\text{SO}_3\text{H}$  groups broken off in the radiolytic step are to appear ultimately as  $\text{SO}_4^{2-}$  ions.

On the other hand, we believe that the increase in  $G(\text{SO}_4^{2-})$  between weight fractions of water of 0.2–0.4 is due to the participation of water radiolysis products bringing about desulfonation. In this range, the measured  $G(\text{SO}_4^{2-})$  is the sum of the contributions of direct and indirect radiolysis:

$$G(\text{SO}_4^{2-}) = G_w f_w + G_R f_R$$

where  $f_w$  and  $f_R$  are the fractions of energy absorbed by the water and resin, respectively, and  $G_w$  and  $G_R$  are the  $G$ -values for the formation of  $\text{SO}_4^{2-}$ -producing species in water (i.e., the  $G$ -value for indirect radiolysis) and for the production of  $\text{SO}_4^{2-}$  by direct radiolysis respectively. From the measured values of  $G(\text{SO}_4^{2-})$  at  $f_w = 0.19$  and  $f_w = 0.43$  it can be calculated that  $G_R = 0.86$  and  $G_w = 1.47$ . Implicit in this calculation is the assumption that in this concentration range all the species react with the resin. Recent work has shown that both electrons and hydroxyl radicals are reactive toward poly(styrene sulfonate) ions<sup>9</sup> and benzene sulfonate ions in aqueous solution.<sup>10</sup> However, it is improbable that all the species reacting with the resin would so react to give  $\text{SO}_4^{2-}$ .

The decline in  $G(\text{SO}_4^{2-})$  at water fractions greater than 0.4 may be ascribed to the increasingly inefficient deposition (as regards  $\text{SO}_4^{2-}$  formation) of energy in the aqueous phase. Thus, water radiolysis products can only contribute to the resin desulfonation if they are able to diffuse to the resin surface before being involved in some other reaction in the aqueous phase. It is obvious that as the amount of water associated with the resin is increased, an increasing proportion of the water radiolysis products will not reach the resin before reacting in some other way. This will manifest itself as the observed decline in  $G(\text{SO}_4^{2-})$  at water fractions greater than 0.4.

#### Effect of Added Scavengers

The resin was also irradiated with aqueous solutions containing methanol, ethanol, and perchloric acid. Table II shows the results of these experiments. Methanol and ethanol were found to depress  $G(\text{SO}_4^{2-})$ , whereas perchloric acid was without effect. Furthermore, inspection of Table II shows that ethanol was a more efficient scavenger than methanol.

TABLE II  
 $\gamma$ -Irradiation of Mixtures of Zeocarb 225 and Water:<sup>a</sup>  
Effect of Added Scavengers on  $G(\text{SO}_4^{2-})$

Scavenger, <i>M</i>	$G(\text{SO}_4^{2-})$		
	Methanol	Ethanol	Perchloric acid
0	0.53	0.53	0.53
1	0.42	0.36	0.55
2	0.36	0.32	0.51
3	0.35	0.30	—
4	0.34	0.27	0.51
5	0.30	0.28	0.54
6	0.29	0.28	0.50

<sup>a</sup> Zeocarb-to-water ratio 1:2 wt/wt.

The simplest explanation of these observations is that methanol and ethanol scavenge the species responsible for the indirect attack. In view of the known reactivities of ethanol and methanol toward hydroxyl radicals,<sup>11</sup> it is probable that it is these species that are responsible for the indirect formation of  $\text{SO}_4^{2-}$  ions. The lack of effect of  $\text{H}^+$  on the course of the radiolysis rules out the possibility that hydrated electrons are involved in reactions producing  $\text{SO}_4^{2-}$  ions.

If this explanation is correct, the measured yield of  $\text{SO}_4^{2-}$  ( $G = 0.28$ ) in the fully scavenged system arises only from the direct radiolysis of the resin. Since in the slurry only 0.31 of the total energy absorption takes place in the resin,  $G(\text{SO}_4^{2-})$  for direct radiolysis corresponds to  $0.28/0.31 = 0.90$ . This is in reasonable agreement with the value of  $G_R = 0.86$  obtained from the water content experiments.

These experiments demonstrate that in interpreting the results of the radiolysis of aqueous slurries of ion-exchange resins, the role of water radiolysis products must be taken into account. Many studies have shown that in general the radiolytic sensitivity of ion-exchange resins is increased in the presence of water. It is possible that energy transfer from the aqueous phase may account for part of this effect. However, the most obvious way in which energy deposited in the water can bring about damage to the resin is by the reactions of the recognized intermediates, hydrated electrons, hydrogen atoms, and hydroxyl radicals. In the case of sulfonic acid resins, it would appear that hydroxyl radicals are the species responsible for indirect radiolytic capacity loss.

We wish to thank the Colombo Plan Authorities and the Saigol Foundation for support for M. K. R. and M. R.

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Received April 30, 1970

Revised May 10, 1970