

# Chemical Communications

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## Electron-scavenger Competition Effect in Radiolysis Systems

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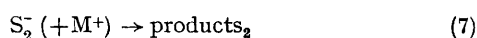
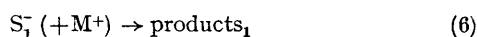
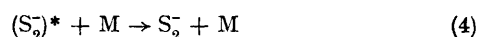
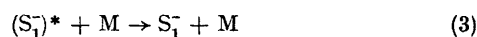
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A RECENT Communication<sup>1</sup> reported that the values of the rate constants of reactions of the hydrated electron determined from pulse radiolysis studies were sometimes different from the values of the relative rate constants determined by studies of competition kinetics.

It has been found that the apparent relative efficiencies of electron scavengers in gas-phase radiolysis systems are sometimes different when scavengers are present in pairs than when they are present singly in a given system. This conclusion was derived from product analysis and steady-state kinetics. Even the single scavenger systems involve competition kinetics, because the electron scavenger must compete with the neutralization reaction if nothing else.

Various concentrations of  $N_2O$ ,  $SF_6$ , and DI were added singly and in pairs to methylcyclohexane vapour at  $110^\circ$  and a total pressure of 380 torr. The values of the ratios of the apparent efficiencies of the scavengers, determined by the single scavenger and the scavenger pair methods respectively are given in the Table. The single scavenger and scavenger pair methods yield relative efficiencies that are different by as much as 20,000-fold. These results can be explained by the

occurrence of the following reactions in a system that contains a pair of scavengers  $S_1$  and  $S_2$ .



where M is some other molecule and  $M^+$  may or may not enter into reactions (6) and (7), depending on the natures of  $S_1^-$  and  $S_2^-$ .

For reaction (5) to occur,  $S_2$  must have a greater electron affinity than has  $S_1$ , and  $S_1^-$  must be sufficiently long-lived to be able to encounter an  $S_2$  and react with it.

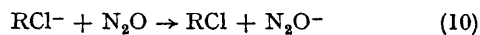
The results indicate that the electron affinities of the present three scavengers are in the order  $DI > SF_6 > N_2O$ . Furthermore, at  $110^\circ$  and 380 torr the half-lives of the negative ions with respect to reaction (6), calculated from the kinetic data by assuming that reaction (5) has a collision efficiency less than or equal to unity, are:  $N_2O^-$ ,  $t_{1/2} \geq 10^{-4}$  sec.;  $SF_6^-$ ,  $t_{1/2} \geq 10^{-7}$  sec. The half-life of  $DI^-$  could not be calculated from the present data because it did not undergo reaction (5), but other information indicates that it is  $> 10^{-3}$  sec. under these conditions.<sup>2</sup>

TABLE

Ratios of apparent efficiencies of electron scavengers in methylcyclohexane vapour at  $110^\circ$  and 380 torr

Method	$\frac{DI}{N_2O}$	$\frac{SF_6}{N_2O}$	$\frac{DI}{SF_6}$
Single scavenger ..	0.1	10	0.01
Scavenger pair ..	2000	200	1.0
Pair/Single..	20,000	20	100

The mechanism suggested earlier<sup>1</sup> to explain the scavenger competition results in aqueous solution should be modified to



where RCl is CCl<sub>4</sub> or CHCl<sub>3</sub>. Thus, in aqueous solution the electron affinity of nitrous oxide is greater than those of carbon tetrachloride and chloroform. Lower limits of the half-lives of CCl<sub>4</sub><sup>-</sup> and CHCl<sub>3</sub><sup>-</sup> in water could have been calculated if the kinetic data had been reported.

It should be possible to observe reaction (5) directly in either the gas or liquid phase, by pulse radiolysis and spectrophotometry, with a suitable pair of scavengers S<sub>1</sub> and S<sub>2</sub>.

If reaction (5) occurs for a given pair of scavengers in the vapour phase, this does not necessarily imply that it will occur with the same pair of scavengers in the liquid phase because the solvation energies of S<sub>1</sub>, S<sub>1</sub><sup>-</sup>, S<sub>2</sub>, and S<sup>-</sup> might alter the energetics of the reaction.

It is hoped that the scavenger competition technique will be useful in determining relative electron affinities of molecules. There is a need for such information both in radiation chemistry and in the field of molecular and electronic structure.

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<sup>1</sup> S. R. Logan and P. B. Wilmot, *Chem. Comm.*, 1966, 558.

<sup>2</sup> J. W. Holtslander and G. R. Freeman, *Canad. J. Chem.*, in the press.