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Electron-scavenger Competition Effect in Radiolysis Systems

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A RECENT Communication[1] 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° 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 efficiences 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.

$$S_1 + e^- \rightarrow (S_1^-)^* \qquad (1$$

$$S_2 + e^- \rightarrow (S_2^-)^* \qquad (2)$$

$$(S_1^-)^* + M \rightarrow S_1^- + M \qquad (3)$$

$$(S_2^-)^* + M \rightarrow S_2^- + M \qquad (4)$$

$$S_1^- + S_2 \rightarrow S_1 + S_2^- \qquad (5)$$

$$S_1^- \ (+M^+) \rightarrow \text{products}_1 \qquad (6)$$

$$S_2^- \ (+M^+) \rightarrow \text{products}_2 \qquad (7)$$

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° 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^-, $t_{\frac{1}{2}} \geqslant 10^{-4}$ sec.; SF_6^-, $t_{\frac{1}{2}} \geqslant 10^{-7}$ 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.[2]

TABLE

Ratios of apparent efficiencies of electron scavengers in methylcyclohexane vapour at 110° *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[1] to explain the scavenger competition results in aqueous solution should be modified to

$$e^-_{aq} + RCl \rightarrow RCl^- \qquad (8)$$

$$RCl^- \rightarrow R + Cl^- \qquad (9)$$

$$RCl^- + N_2O \rightarrow RCl + N_2O^- \qquad (10)$$

$$e^-_{aq} + N_2O \rightarrow N_2O^- \qquad (11)$$

$$N_2O^- \rightarrow N_2 + O^- \qquad (12)$$

where RCl is CCl_4 or $CHCl_3$. 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_4^- and $CHCl_2^-$ 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_1 and S_2.

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_1, S_1^-, S_2, and S^- 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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[1] S. R. Logan and P. B. Wilmot, *Chem. Comm.*, 1966, 558.

[2] J. W. Holtslander and G. R. Freeman, *Canad. J. Chem.*, in the press.