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DETRITIATION IN 1,8-DIMETHYLNAPHTHALENE, ACENAPHTHENE AND PERINAPHTHANE

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We reported recently[1] the rates of detritiation of 1,8-dimethylnaphthalene, acenaphthene and perinaphthane in anhydrous trifluoroacetic acid at 30°. Subsequently Ansell and Taylor[2] drew attention to the fact that we had discussed our results in terms of rate constants rather than partial rate factors; on the basis of one experimental activation energy (for[5-T]-acenaphthene) they extrapolated our rate constants to 70° and re-interpreted our data. The partial rate factors which they derive from our results in this way are subject to uncertainties which, far from being of 'inconsequential magnitude', are so large as to make their discussion quite misleading. We are concerned lest their extrapolated partial rate factors become incorporated into the literature as reliable values, and we offer comment on their analysis.

Ansell and Taylor convert our rate constants measured at 30°, to values for 70°, using $E_a = 71.5$ kJ.mol^{-1} determined for [5-T]-acenaphthene, the most reactive of the nine positions. We know that E_a values for hydrogen-exchange in polymethylbenzenes at 70° can vary widely; Wilkinson[3] has obtained values for [3-T]-pseudocumene (k_{70},0.0016s^{-1}; E_{act}70.2 kJ.mol^{-1}), [5-T]-pseudocumene (0.0027; 68.3), [4-T]-isodurene (0.25; 59.6), and [6-T]-pentamethylbenzene (0.7; 56.9). Taylor himself reports[4] E_a values of 78.7 and 84.9 kJ.mol^{-1} for the 1- and 2- positions in naphthalene. Our substrates cover a wider reactivity range ($\sim 10^5$ in k) and we can therefore assign to them reasonable upper and lower activation energy limits of, say, 60 and 80 kJ.mol^{-1}; extrapolating our rate constants to 70° using these two values gives partial rate factors (relative to $k_{benzene} = 9.5\times10^{-9}$ s^{-1} at 70°) shown in the Table.

We believe Ansell and Taylor's assumption of a constant E_a to be quite unjustified. As the data in the Table show, no reliance can be placed on comparisons of partial rate factors derived in this way with values calculated assuming additivity. It was for this reason that we originally carried out a linear analysis of our data[1]; while we agree with Ansell and Taylor that a free energy analysis is to be preferred, it is clear from our Table that almost any conclusion can be supported by suitable combination of activation energies.

TABLE

Partial rate factors for protodetritiation at 70°.

Substrate	$10^{-3}f$ (E_a 60kJ.mol^{-1})	$10^{-3}f$ (E_a 80kJ.mol^{-1})
[2-T]-1,8-dimethylnaphthalene	64.2	162
[3-T]-1,8-dimethylnaphthalene	0.95	2.4
[4-T]-1,8-dimethylnaphthalene	119	300
[3-T]-acenaphthene	867	2,190
[4-T]-acenaphthene	1.60	4.0
[5-T]-acenaphthene	E_a = 71.5, $10^{-3}f$ = 3970	
[4-T]-perinaphthane	159	402
[5-T]-perinaphthane	0.71	1.8
[6-T]-perinaphthane	462	1,170

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