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SELECTIVITY OF BRIDGEHEAD RADICALS

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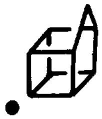
At temperatures above 335 K, the homocubyl radical 1 reacts with greater selectivity than the adamantyl radical 4, as was shown by Rüchardt in studies using competition system BrCCl$_3$/CCl$_4$.[1] The competition constants k_{Br}/k_{Cl} of bicyclic bridgehead radicals 2 and 3 are between those of 1 and 4.[1] Recently, Stock has observed that at 353 K cubyl radical 5 is as selective as 1 and more selective than 4, too.[2]


1


2

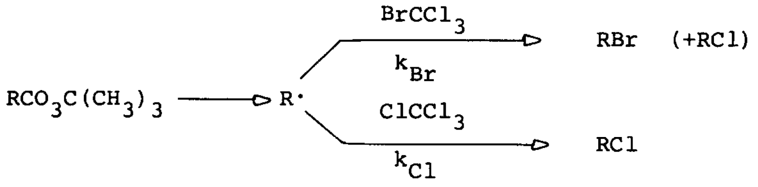

3


4


5

This order of selectivity is extremely surprising, because front strain increases[3] and internal strain decreases[4] when going from homocubyl radical 1 or cubyl radical 5 via 2 and 3 to adamantyl radical 4. Reasonably, one would expect radical reactivity to decrease in this order[5] and, according to the selectivity principle, selectivity to increase.[6] Owing to this contrast between expected order of selectivity and experimental values, we decided to study the temperature dependence of the competition constants of bridgehead radicals 1 to 4.

The radicals were generated from peresters in large excess of $BrCCl_3$ and CCl_4.



$(C_6H_5)_3CH$ was added to trap most of $Cl_3C·$ and $(CH_3)_3CO·$ radicals. According to literature procedure the small amount of RCl formed from $BrCCl_3$ in absence of CCl_4 was taken into account.[1] Temperature dependence measurements of selectivities between 323 and 413 K afford a fan of straight lines (Figure 1) which meet at the isoselective temperature T_{is}[6] of about 230 K. Below this isoselective temperature the radicals adopt expected order of selectivity, i.e. the adamantyl radical 4 is the most selective, the homocubyl radical 1 the least selective of bridgehead radicals 1 - 4. Thus, interpretation of their selectivities is possible only when this temperature dependence is taken into account. Interpretation can be simplified by using temperature independent selectivity values. Activation parameters determined between 323 and 423 K are shown in Table I.

Table I

Activation enthalpy and activation entropy differences of bridgehead radicals in competition system $BrCCl_3/CCl_4$.

Radical	$\Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}$ a) $kJ·mol^{-1}$	$\Delta S^{\ddagger}_{Cl} - \Delta S^{\ddagger}_{Br}$ b) $J·mol^{-1}·K^{-1}$
1	2.1	-29
2	4.2	-20
3	4.8	-16
4	5.5	-11

a) Standard deviation ± 10%. b) Standard deviation ± 3 $J·mol^{-1}·K^{-1}$

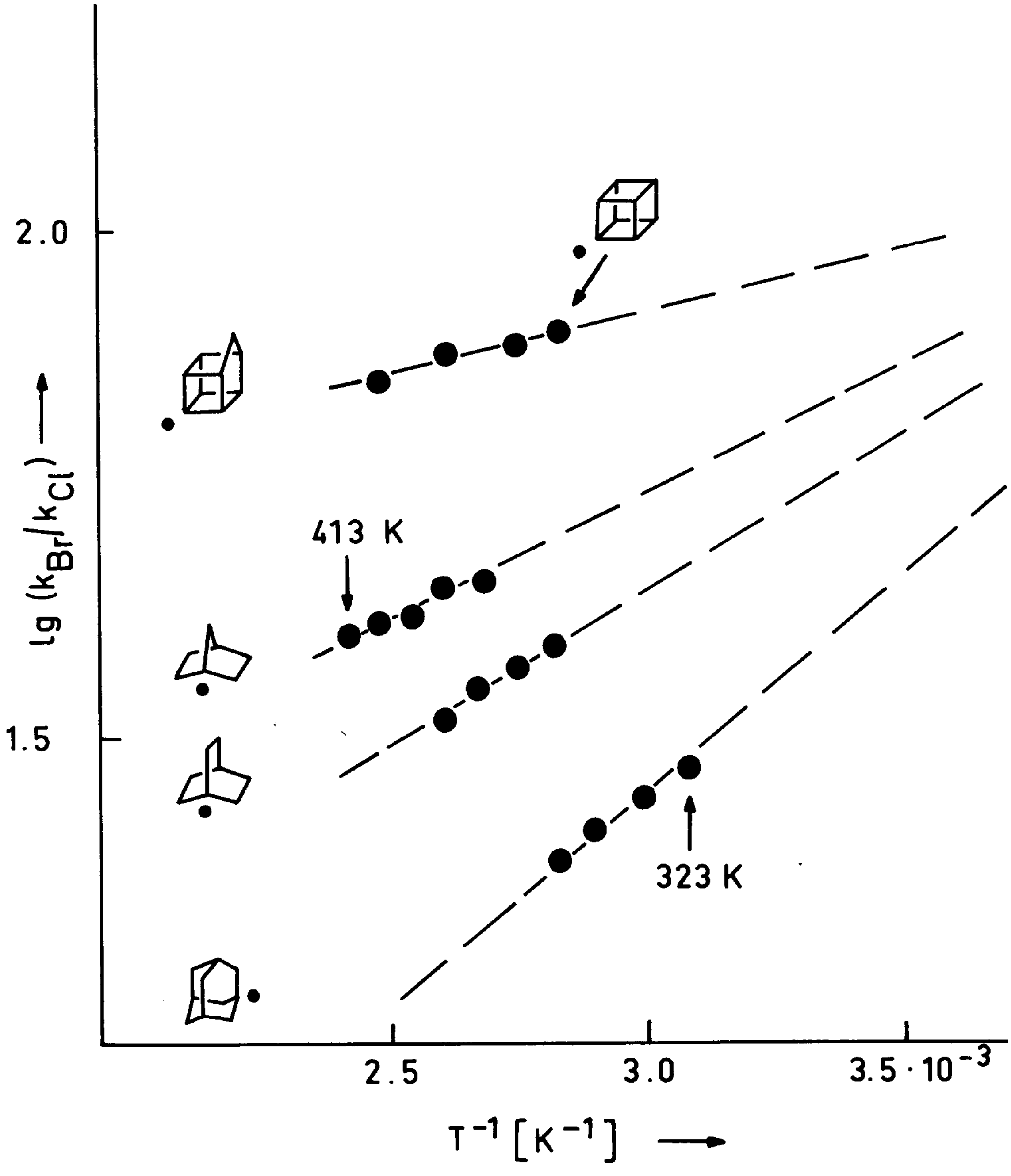


Figure I. Temperature dependence of selectivities lg(k_{Br}/k_{Cl}) of bridgehead radicals using competition system $BrCCl_3/CCl_4$. The experimental value of the cubyl radical at 353 K, cited from ref. 2, fits onto the selectivity line of the homocubyl radical.

The activation enthalpy difference of the homocubyl radical 1 amounts to only 2.1 $kJ \cdot mol^{-1}$, but the values increase via 4.2 (radical 2) and 4.8 (radical 3) to 5.8 $kJ \cdot mol^{-1}$ (adamantyl radical 4). Thus, while front strain increases[3] and internal strain decreases[4] in the order 1-4, there is an increase in the difference of activation enthalpies of the chloride and bromide abstraction from $XCCl_3$ (X=Cl,Br). This order of activation enthalpies meets expectation. The unexpected order of selectivity in Figure 1 is caused only by exceeding the isoselective temperature.[7]

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References and Notes

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2) T.Y.Luh and L.M.Stock, *J. Org. Chem.* **43**, 3271 (1978).
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4) R.C.Bingham and P.v.R.Schleyer, *J. Am. Chem. Soc.* **93**, 3189 (1971).
5) The rate of formation of the radicals increases from 1 and 2 via 3 to 4. See ref. 1 and 2.
6) B.Giese, *Angew. Chem.* **89**, 162 (1977); *Angew. Chem. Int. Ed. Engl.* **16**, 125 (1977).
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