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HYDROGEN ATOM TRANSFER IN THE REACTIONS OF THERMALLY-GENERATED DI-t-ALKYLKETYL AND 1-ADAMANTYL RADICALS

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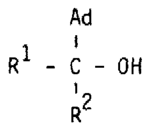
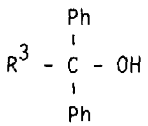
ABSTRACT.- In the thermolysis of tri-(1-adamantyl)methanol about 55% of the di-(1-adamantyl)-ketyl and 1-adamantyl radicals escape from the solvent cage, the former transferring hydrogen to benzophenone and the second abstracting hydrogen from the solvent, toluene, with isotope effects on the latter reaction consistent with tunnelling.

Hydrogen atom transfer from a ketyl radical, generally hydroxyalkyl, to a carbonyl compound (aryl ketone or aldehyde) has been observed in both photochemical[1] and thermally-induced[2] radical reactions. Preliminary work in this laboratory[3] showed that aryl-t-alkylketones were reduced by di-t-alkylketyl and t-alkyl radicals produced in the rate-determining step of tri-t-alkyl-methanol thermolysis,[4,5] clearly indicating hydrogen transfer but equivocal as to which radical was losing this atom to the ketone.

We wish now to report that in the presence of benzophenone (BP) the thermolysis of tri-(1-adamantyl)methanol[5] (Ad_3COH, **1a**) in toluene, a hydrogen donor solvent (SL, where L = H or D) gives only adamantane (AdL), bibenzyl (S_2), benzhydrol (BPH_2), benzophenone-solvent cross-product (BPSH, **2a**) and di-(1-adamantyl)ketone (Ad_2CO)[6] (Table I). The adamantane arises partly in the cage reaction of Ad˙ with the di-(1-adamantyl)ketyl radical (Scheme : process 2) while the fraction[7] of Ad˙ which escapes from the cage abstracts hydrogen from the solvent methyl group to give benzyl radical (process 3). The ketyl radical is scavenged by the benzophenone (process 4), with formation of the benzophenone ketyl radical, $Ph_2C^{\cdot}OH$ (denoted BPH˙).


$$R^1-\overset{\displaystyle Ad}{\underset{\displaystyle R^2}{C}}-OH$$

1a : $R^1 = R^2 = Ad$
1b : $R^1 = Ad;\ R^2 = Nor$
1c : $R^1 = R^2 = Nor$


$$R^3-\overset{\displaystyle Ph}{\underset{\displaystyle Ph}{C}}-OH$$

2a : $R^3 = S$ = benzyl
2b : $R^3 = Ad$

The normal reactions of $Ad_2C^{\cdot}OH$, to form secondary alcohol and the cross-product Ad_2SCOH[5], are totally suppressed by BP. It seems only reasonable therefore to assume that reaction of Ad˙ with $Ad_2C^{\cdot}OH$ outside the cage is also suppressed. Notably absent (less than 1%) from the thermolysis of **1a** with BP in toluene are (1-adamantyl)toluenes, 1-benzyladamantane and 1,1'-bi-adamantyl, all products from the photolysis of azo-1-adamantane in toluene.[8] Side-chain hydrogen abstraction is manifestly faster than ring-attack under thermolysis conditions ; radicals Ad˙ and S˙ do not coexist long enough to react, the second being formed at the expense

SCHEME

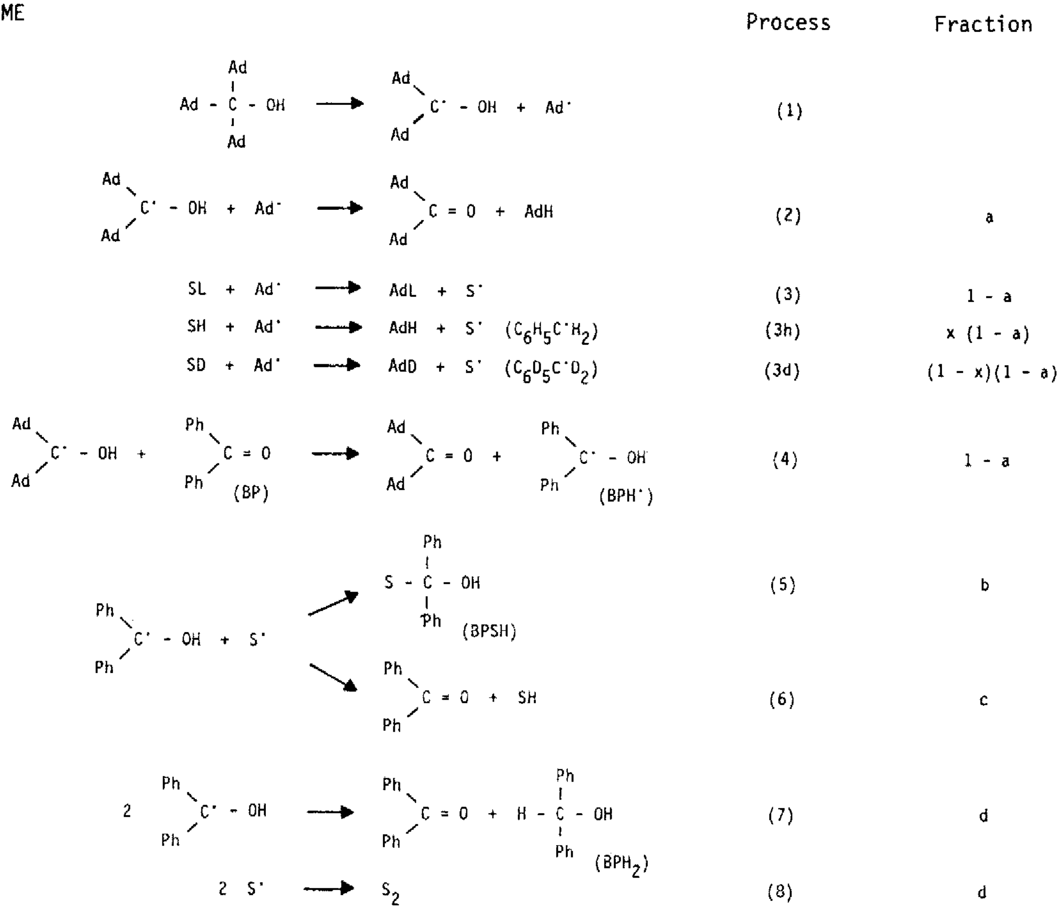


TABLE I : Fractional product yields for the thermolysis of Ad_3COH with equimolar benzophenone in toluene-h_8/d_8 mixtures (relative to Ad_2CO = 1.00 ; no significant variation in yields with [tol-h_8] / [tol-d_8] from 0.00 to 0.99).

T°C	AdL	S_2 (d)	BPSH (b)
165	0.98 ± 0.05	0.067 ± 0.006	0.306 ± 0.010
145	1.03 ± 0.05	0.059 ± 0.005	0.280 ± 0.009
185	1.00 ± 0.06	0.068 ± 0.003	0.303 ± 0.006

of the first ; finally, Ad˙ radicals react with solvent rather than with each other. The further absence of the possible cross-product Ph_2AdCOH, **2b**, indicates that BPH˙ and Ad˙ do not react or, more probably, do not coexist. The fact that the yields of **2a** and S_2 are virtually unaffected by solvent deuteriation (Table I) strongly suggests that, once $Ad_2C^{\cdot}OH$ and Ad˙ have escaped from the cage, the system evolves as though the only reactive species were BPH˙ and S˙, the cross-product predominating.[9] Processes 3 and 4 must therefore be faster than all potential competing reactions.

Thermolysis of **1a** in mixtures of normal toluene and toluene-d_8, followed by determination of the deuterium content of the bibenzyl and adamantane,[10] leads to the kinetic isotope effect for hydrogen abstraction from toluene by Ad· and to an estimate of the magnitude of the cage effect (Table II). For example, the C_7H_7/C_7D_7 ratio at 165°C divided by the molar ratio of normal and deuterated toluene gives k_H/k_D values in the range 5.75-6.28 (mean of 5 determinations : 6.07 ± 0.20). Considering H and D abstraction separately (processes 3h and 3d, where $x/(1 - x) = k_H\,[\text{tol-}h_8]\,/k_D\,[\text{tol-}d_8]$) we can calculate the cage effect, a, from the experimental AdH/AdD ratios :[11]

$$\frac{\mathrm{AdH}}{\mathrm{AdD}} = \frac{a + x(1 - a)}{(1 - x)(1 - a)}\ , \text{ whence } \%\mathrm{AdH} = 100\ a(1 - x) + x \qquad \text{eqn. 1}$$

Balancing S· formation and consumption, we have : $(1 - a) = b + c + 2d$ eqn. 2

where b and d are known from the yields of cross-product and bibenzyl, respectively. Fraction c (process 6) can thus be calculated (Table II). The observed cage effect is found to vary *somewhat erratically with temperature* ; *the precision of the measurements* allows us to say only that it is about 0.45 for **1a** in this temperature range and that c is about 0.12, which makes the disproportionation/combination ratio for BPH· and S· roughly 0.4.

TABLE II : Product isotope effects for bibenzyl and adamantane in the thermolysis of Ad_3COH with equimolar benzophenone in toluene-h_8/d_8 mixtures.

$\frac{[\text{tol-}h_8]}{[\text{tol-}d_8]}$	(T = 145°C) C_7H_7/C_7D_7	(T = 145°C) %AdH[a]	(T = 165°C) C_7H_7/C_7D_7	(T = 165°C) %AdH[b]	(T = 185°C) C_7H_7/C_7D_7	(T = 185°C) %AdH[c]
0.111	0.71	69.4 (70.1)	0.64	70.1 (68.4)	0.59	64.2 (63.9)
0.250	1.75	81.9 (80.6)	1.52	79.0 (79.0)	1.34	74.2 (75.4)
0.425	3.13	85.6 (86.6)	2.67	83.4 (85.2)	2.30	82.0 (82.5)
0.673	4.69	91.0 (90.7)	4.06	88.5 (89.6)	3.65	87.3 (87.5)
0.992	6.88	92.3 (93.3)	6.17	90.0 (92.5)	5.71	92.2 (91.0)

[a] calculated values (in parentheses) based on $k_H/k_D = 6.94$; a = 0.47 ± 0.02, c = 0.13 ± 0.04

[b] $k_H/k_D = 6.07$; a = 0.47 ± 0.02, c = 0.08 ± 0.04

[c] $k_H/k_D = 5.44$; a = 0.42 ± 0.02, c = 0.14 ± 0.03

Kinetic isotope effects on hydrogen abstraction by Ad· from toluene were also measured at higher temperature by studying the thermolysis of **1b** and **1c** (Nor = 1-norbornyl), less reactive analogs of **1a**.[5] The extreme values for the series **1a-c** are 6.9 and 3.9 at 145°C and 320°C, respectively. Plotting $\ln(k_H/k_D)$ against 1/T°K gives $A_H/A_D = 1.14$ and $E_a^D - E_a^H = 1.47$ kcal.mol^{-1}

Extrapolation to 65°C provides a value of 10.2 in good agreement with those found for the photochemically-initiated reaction (9.2 and 11.4).[8] These results are therefore consistent with tunnelling, though only two of the four criteria are satisfied (high isotope effects and $E_a^D - E_a^H$ greater than 1.15). The A_H/A_D value is within the classical limits (0.5 - 1.41) and no curvature of the Arrhenius plot is detectable.[12]

Further work will be directed towards the investigation of other t-alkyl radicals, particularly t-butyl.

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6. Aliquots of **1a** and BP (both 0.006M) in toluene-h_8/d_8 mixtures (toluene-d_8 was Aldrich 99+ atom % D) were sealed under vacuum in pyrex glass tubes after 3-4 freeze-pump-thaw cycles. After 10 reaction half-lives the products were analysed by GC on packed SE30 (yields) or capillary CP-Sil 5 (labelling measurements) columns. BPH_2 was detected by capillary GC but not determined.
7. Since a given radical can undergo various reactions, in the Scheme each process is associated with a certain fraction : for Ad˙ and $Ad_2C^{\cdot}OH$ the totals must be unity while, for the other radicals, the processes by which they are formed and consumed must balance.
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10. On capillary GC bibenzyl appears as three partly-resolved peaks corresponding, in order of elution, to bibenzyl-d_{14}, -d_7h_7 and -h_{14}. The relative amounts of C_7H_7 and C_7D_7 were determined by integrating the ITD intensities at m/e 91, 98, 182, 189 and 196. AdH/AdD ratios were determined by the method of Engel.[8] Ion Trap Detector measurements were performed on a FinniganMAT ITD 800B apparatus.
11. Since eqn. 1 is particularly sensitive to errors on the high AdH values, a was calculated by minimizing $\Sigma\ (AdH_{obs} - AdH_{calc})^2$.
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