Reactions of Thermally Generated 1-Adamantyl and Di(1-adamantyl)ketyl Radicals in Toluene

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Thermolysis of tri(1-adamantyl)methanol in toluene at 145–185 °C gives bibenzyl, di(1-adamantyl) ketone, di(1-adamantyl)methanol and a cross-product, 1,1-di(1-adamantyl)-2-phenylethanol, in yields which depend on the temperature and the isotopic composition of the solvent. In the presence of benzophenone the intermediate di(1-adamantyl)ketyl radical transfers hydrogen, giving ketone and the hydroxybenzhydryl radical, the cross-product then being 1,1,2-triphenylethanol. The cage effect (0.38–0.415) has been determined by studying thermolysis in deuterium-labeled toluene. In normal toluene almost all the secondary alcohol is formed from $Ad_2C^{\bullet}OH$ by hydrogen abstraction from the solvent, whereas in deuteriated toluene 22–32% results from self-disproportionation of ketyl radicals, showing that there is a substantial kinetic isotope effect on hydrogen abstraction. Kinetic modeling of the reaction by means of a rapid, iterative procedure based on the steady-state approximation suggests values in the range 6.0–7.4, decreasing as the temperature rises.

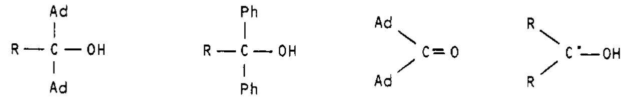
That tri-*tert*-alkylmethanols undergo thermolysis with formation of ketones and secondary alcohols by loss of one of the *tert*-alkyl groups has been known for some 15 years now.[1] Steric effects upon the reactivity of alcohols of this type can readily be interpreted in terms of the strain energy difference between the initial tertiary alcohol and the corresponding secondary alcohol, this latter being a reasonable surrogate for the thermolysis transition state.[2] The products of alcohol thermolysis have not been studied systematically, though it was shown that for alcohols with bridgehead *tert*-alkyl groups only, the number of processes likely to occur after the rate-determining step is relatively limited.[2b]

Important amongst these processes are hydrogen abstraction from the solvent by the *tert*-alkyl and the di-*tert*-alkylketyl radicals, followed by reaction of the solvent-derived radicals with each other or with the two precursors, particularly the ketyl radical. While the self- or cross-reactions of small radicals are often diffusion controlled,[3] those of encumbered tertiary alkyl radicals are so slow that such radicals are described as "persistent".[4] Whereas the *tert*-alkyl radical clearly falls into the first category, the di-*tert*-alkylketyl radical might be placed in the second, were it not for the hydroxy group with its easily transferable hydrogen atom. Little appears to be known about the reactivity of such species.

The aim of the present work was to disentangle from the several possible processes those which contribute significantly to the overall reaction occurring after C–C bond scission in thermolysis. Tri(1-adamantyl)methanol,[5] **1a**, was chosen for this study for several reasons: it is thermolyzed at fairly low temperatures, the resulting radicals do not rearrange, and the product composition is particularly simple. By studying the reaction in normal and deuteriated toluene it has been possible to evaluate the contributions of the elementary processes, which are then simulated by kinetic modeling. A rapid, iterative procedure based on the steady-state approximation has been devised for this purpose.

Scheme I

Process	Fraction	Rate const.	
$Ad_3COH \longrightarrow Ad_2C^{\bullet}OH + Ad^{\bullet}$	1.0	k_1	(1)
$Ad_2C^{\bullet}OH + Ad^{\bullet} \longrightarrow AdH + Ad_2CO$	a	k_2	(2)
$SL + Ad^{\bullet} \longrightarrow AdL + S^{\bullet}$	(1 - a)	k_3	(3)
$SL + Ad_2C^{\bullet}OH \longrightarrow Ad_2CLOH + S^{\bullet}$	b	k_4	(4)
$2\ Ad_2C^{\bullet}OH \longrightarrow Ad_2CHOH + Ad_2CO$	c	k_5	(5)
$S^{\bullet} + Ad_2C^{\bullet}OH \longrightarrow Ad_2SCOH$	d	k_6	(6)
$S^{\bullet} + Ad_2C^{\bullet}OH \longrightarrow Ad_2CO + SH$	e	k_7	(7)
$2\ S^{\bullet} \longrightarrow S_2$	f	k_8	(8)



1a : R = Ad
1b : R = H or D
1c : R = benzyl

2a : R = benzyl
2b : R = Ad

3

4a : R = Ph
4b : R = Ad

Results

Thermolysis Products. The products of the thermolysis of tri(1-adamantyl)methanol, **1a**, in toluene (SL, where L = H or D) are, in order of GC elution on SE30, adamantane, bibenzyl, di(1-adamantyl)ketone, **3**, di(1-adamantyl)methanol, **1b**, and the cross-product (CP), 1,1-di(1-adamantyl)-2-phenylethanol, **1c**. It can be seen from Table I that the product composition depends on the temperature, with the secondary alcohol yield decreasing and that of the cross-product increasing with rise in temperature. In octadeuteriotoluene the same trend is followed, but the secondary alcohol yield is approximately halved while that of **1c** increases slightly. It will be noted that the yields in normal toluene are sensitive to the initial alcohol concentration; the lower it is, the more secondary alcohol and the less cross-product are formed.

On the basis of the products observed and it being assumed that the 1-adamantyl radical does not transfer

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(1) Lomas, J. S.; Dubois, J. E. *J. Org. Chem.* **1974**, *39*, 1776.

(2) (a) Lomas, J. S.; Dubois, J. E. *J. Org. Chem.* **1982**, *47*, 4505. (b) Lomas, J. S. *J. Org. Chem.* **1985**, *50*, 4291. (c) Lomas, J. S. *Acc. Chem. Res.* **1988**, *21*, 73.

(3) Landolt-Börnstein, New Series, Group II. *Radical Reaction Rates in Liquids*; Fischer, H., Beckwith, A. L. J., Griller, D., Lorand, J. P., Eds.; Springer: Berlin, 1984; Vol. 13a.

(4) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1976**, *9*, 13.

(5) Lomas, J. S. *Nouv. J. Chem.* **1984**, *8*, 365.

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Table I. Thermolysis of Tri(1-adamantyl)methanol in Toluene: Solvent Isotope, Temperature, Benzophenone, and Concentration Effects upon Relative Molar Product Composition (%)

temp, °C	solv[a]	concn, 10^{-3} M	[BP]/[**1a**]	bibenzyl	Ad_2CO[b]	Ad_2CLOH[b]	CP, **1c**	CP, **2a**	AdL[b]
145	H	6.25		36.2	56.1	37.4	6.5		
165	H	6.25		31.1	58.0 (56)	32.3 (33)	9.7		(95)
165	H	6.25	0.1	24.3	68.9 (65)	24.8 (26)	6.3	8.3	(95)
165	H	6.25	0.2	17.7	80.5 (76)	16.6 (18)	2.9	17.4	(94)
165	H	6.25	0.3	9.7	92.8	6.6	0.6	25.4	
165	H	6.25	0.4	6.1	98.8 (95)	1.2 (2)	0.0	30.6	(94)
165	H	6.25	0.5	5.8	99.4	0.6	0.0	30.7	
165	H	6.25	0.6	5.8	99.7	0.3	0.0	30.3	
165	H	6.25	0.8	5.6	99.9	0.1	0.0	31.2	
165	H	6.25	1.0	5.9	99.8 (96)	0.2 (0)	0.0	30.9	(93)
165	H	6.25	2.0	5.8	100.0 (97)	0.0 (0)	0.0	31.0	(96)
165	H	3.10		34.6	56.6	35.9	7.5		
165	H	1.56		36.9	55.1	38.5	6.4		
185	H	6.25		27.0	60.2	28.5	11.3		
145	D	6.25		16.4	70.3	18.1	12.5		
145	D	6.25	1.0	5.2	100.0	0.0	0.0	29.8	
165	D	6.25		14.6	71.1	15.2	13.7		
165	D	6.25	1.0	6.5	100.0	0.0	0.0	31.7	
185	D	6.25		12.8	71.1	13.9	15.0		
185	D	6.25	1.0	6.8	100.0	0.0	0.0	29.8	

[a] D denotes toluene-d_8, H toluene-h_8. [b] Absolute yields with respect to **1a** given in parentheses.

Scheme II

Process		Fraction	
$BP + Ad_2C^{\bullet}OH$	$\longrightarrow Ad_2CO + BPH^{\bullet}$	$(1 - a)$	(9)
$2\ BPH^{\bullet}$	$\longrightarrow BP + BPH_2$	c'	(5')
$S^{\bullet} + BPH^{\bullet}$	$\longrightarrow BPSH$	d'	(6')
$S^{\bullet} + BPH^{\bullet}$	$\longrightarrow BP + SH$	e'	(7')

hydrogen to any species, the overall reaction can be completely described by the various processes shown in Scheme I. Since a given radical can be involved in more than one process, each process is associated with a certain fraction of the overall reaction, indicated in the scheme.

Hydrogen Transfer to Benzophenone. Preliminary work in this laboratory showed that aryl-*tert*-alkyl ketones were reduced by the di-*tert*-alkylketyl and *tert*-alkyl radicals produced in tri-*tert*-alkylmethanol thermolysis.[6] When **1a** is thermolyzed in the presence of benzophenone, however, reduction to benzhydrol is a minor process. The most important features are that the di(1-adamantyl)methanol, **1b**, yield falls to zero and that the original cross-product, **1c**, is replaced by a new one, 1,1,2-triphenylethanol, **2a**, obviously formed by combination of the benzyl radical with the hydroxybenzhydryl radical (benzhydrol radical or benzophenone ketyl radical), denoted $BPH^{\bullet}$, **4a**, in about 31% yield. These changes follow the benzophenone (BP) concentration linearly: at 165 °C the yield of ketone rises from 58% to 99–100%, that of bibenzyl falls from 31% to 6%, and that of **1c** from 10% to zero as **2a** rises from zero to 31% (Figure 1). The intersection of the rise or fall of any product (except **1c**, which is slightly curved) and the horizontal, indicating that there is no further significant change, is situated at a BP/**1a** ratio of 0.37 mol/mol. Clearly, a hydrogen atom is transferred from the di(1-adamantyl)ketyl radical, $Ad_2C^{\bullet}OH$, **4b**, to benzophenone (Scheme II, process 9) so rapidly that the customary reactions of **4b** are blocked. In Scheme II, process 9 replaces process 4 of Scheme I and processes 5'–7' are substituted for the analogous processes 5–7; the others are unaffected.

Since the addition of further amounts of BP beyond a mole ratio of about 0.4 has no significant effect upon the product composition it would appear that a substantial fraction of the $Ad_2C^{\bullet}OH$ reacts before encountering BP, the most plausible hypothesis being that it reacts with the $Ad^{\bullet}$ radical inside the solvent cage. While it could conceivably react with $Ad^{\bullet}$ outside the cage, it seems highly unlikely that this particular reaction would take place when the others are totally suppressed. The processes appearing in Schemes I and II can be summarized then in the diagram below. That occurring inside the cage should be independent of what happens outside, while the rest must respond to changes in the concentration of alcohol and BP (or any other additive), in the solvent and the temperature.

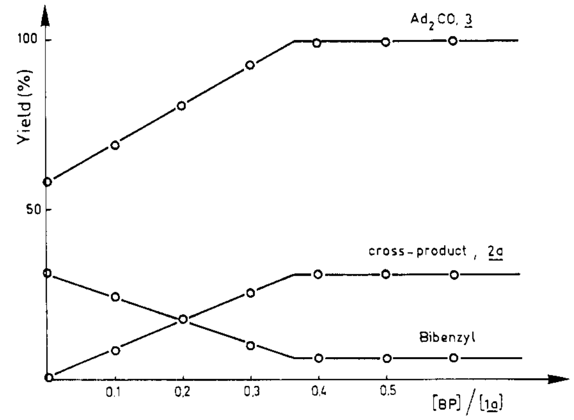
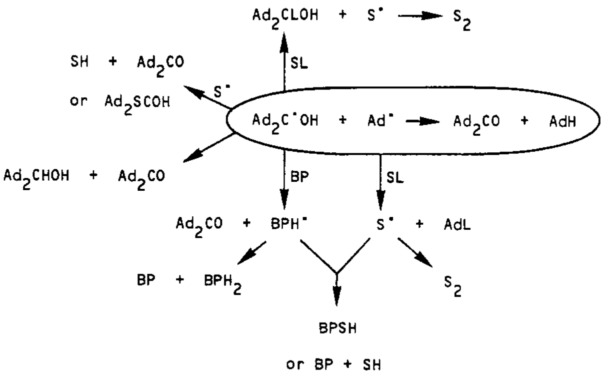


Figure 1. Thermolysis of tri(1-adamantyl)methanol: dependence of product composition on the benzophenone/alcohol mole ratio (**1a** initially 6.25 × 10^{-3} M).



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[6] Boussad, N., D.E.A. Thesis, University of Paris 7, 1987.

Table II. Thermolysis of Tri(1-adamantyl)methanol in Toluene: Cage Effects and Breakdown of Fractional Yields in Terms of Contributing Processes

temp, °C	solv[a]	cage eff (*a*)	FY-CLOH (*b* + *c*)	*b*/*c*	(*b*)[b]	(*c*)[b]	FY-CP (*d*)	FY-S_2 (*f*)	FY-CO	(*e*)	*e*/*d*
145	D	0.415	0.181	3.7	0.135	0.037	0.125	0.164	0.703	0.253[c]	2.02
165	D	0.40	0.152	2.6	0.107	0.042	0.137	0.146	0.711	0.277[c]	1.99
185	D	0.38	0.139	2.1	0.090	0.043	0.150	0.128	0.711	0.294[c]	1.96
145	H	0.415	0.374		0.346	0.021	0.065	0.362	0.561	0.131[d]	
165	H	0.40	0.323		0.315[e]	0.000[e]	0.097	0.311	0.580	0.194[d]	
185	H	0.38	0.285		0.265	0.010	0.113	0.270	0.602	0.221[d]	

[a] D denotes toluene-d_8, H toluene-h_8. [b] Calculated from mean of FY-CLOH (*b* + *c*) and FY-S_2 (*f*). [c] Mean of values from eq 3–5. [d] From FY-CP and appropriate *e*/*d* from above. [e] Solutions with *c* less than zero rejected.

The Cage Effect and Benzophenone Consumption. When **1a** is thermolyzed in toluene-d_8, the adamantane formed by hydrogen (protium) transfer from $Ad_2C^\bullet OH$ within the cage will be normal, whereas that arising from hydrogen (deuterium) abstraction from the solvent will be deuteriated at the 1-position. The extent of 1-d labeling of the adamantane is therefore a direct measure of the cage effect or, to be more exact, of its complement $(1 - a)$. As expected, the cage effect decreases slightly as the temperature increases, from 0.415 at 145 °C to 0.38 at 185 °C, but is not affected by the presence of benzophenone. This last result is important in that it shows clearly that the cage effect does not depend on the molecules which make up the cage. In what follows we shall assume, therefore, that it does not depend on the isotopic labeling of the solvent either. This means that at 165 °C, for example, some 60% of the radicals are escaping from the solvent cage, yet only about 37% apparently react with BP. However, this paradox ignores the fact that processes 5′ and 7′ regenerate BP from **4a**. The contribution of process 7′, the disproportionation of benzyl and hydroxybenzhydryl radicals, in normal toluene containing excess BP, is obtained by balancing $S^\bullet$ formation and consumption:

$$(1 - a) = d' + e' + 2f \qquad (1)$$

where d' and f are known from the yields of triphenylethanol and bibenzyl, respectively. At 165 °C this means that e' is about 0.17 and the disproportionation/combination ratio 0.55; corresponding values at 145 and 185 °C are 0.72 and 0.62, respectively.[7] Applying the same procedure to $BPH^\bullet$, we have:

$$(1 - a) = d' + e' + 2c' = (c' + d') + (c' + e') \qquad (2)$$

which requires that the yield of benzhydrol be the same as that of bibenzyl under these conditions. Comparison of the benzylic CH_2 ^1H NMR signals in **2a** and bibenzyl with the nonaromatic CH in benzhydrol gave a slightly lower value (3–4% as compared to 6% of bibenzyl), suggesting a very small contribution from side reactions not considered in the scheme. Equation 2 can be expressed as follows: the term $(1 - a)$ is the fraction of $Ad_2C^\bullet OH$ which escapes from the cage and is scavenged by BP; $(c' + d')$ is that part of the resulting $BPH^\bullet$ which is converted into identifiable products (but for the missing 2–3%), while $(c' + e')$ reappears as benzophenone. Consequently, only 31 + 6 = 37 mol % of BP per mole of **1a** is consumed, the rest being recycled, thus accounting for the ceiling value.

Deuterium Isotope Effect on Product Distribution. We can now proceed to analyze the product data for the thermolysis of **1a** in toluene without BP or any other radical trap (Scheme I). As noted above, the outstanding effect of solvent deuteriation is to halve the secondary alcohol yield, which is consistent with there being a significant isotope effect upon hydrogen abstraction from the solvent by $Ad_2C^\bullet OH$ (process 4). However, the overall reaction must be broken down into its component parts before a number can be put to this statement. We first write four equations for the formation and consumption of $Ad_2C^\bullet OH$ and $S^\bullet$, and for the fractional yields (FY) of ketone **3** and alcohol **1b**:

$$\text{for } S^\bullet\text{:} \quad (1 - a) + b = d + e + 2f \qquad (3)$$

$$\text{for } Ad_2C^\bullet OH\text{:} \quad (1 - a) = b + 2c + d + e \qquad (4)$$

$$\text{ketone: } \text{FY-CO} = a + c + e \qquad (5)$$

$$\text{secondary alcohol: } \text{FY-CHOH} = b + c \qquad (6)$$

Obviously, the FYs of the cross-product, **1c**, and of bibenzyl are d and f, respectively. Manipulation of eq 3 and 4 gives: $f = (b + c)$, that is, the bibenzyl and secondary alcohol yields should be the same. This equality is approximately satisfied at all three temperatures in both normal and deuteriated solvent, with the bibenzyl yield generally 1–2% below that of the alcohol. Though small enough to be attributed to experimental error, this may mean that a very small amount of benzyl radical also is lost in side reactions, possibly reaction with residual oxygen or hydrogen abstraction from trace impurities in the solvent.

Let us now consider the reaction in toluene-d_8. The cage effect, a, is known and the values of b and c can be calculated from the deuterium content of the secondary alcohol. This is deuteriated on the C–OH carbon or not, depending on whether it is formed by hydrogen abstraction from the solvent or by disproportionation of two ketyl radicals. Taking the data at 165 °C, for example, we have two equivalent estimates of $(b + c)$, the **1b** and bibenzyl yields. From the average and the b/c ratio determined by GC/MS we obtain: $c = 0.042$ and $b = 0.107$. Now, eq 3–5 contain only one unknown, e, pertaining to the disproportionation of $S^\bullet$ with $Ad_2C^\bullet OH$ (process 7), which therefore has a mean value of 0.272, whence the disproportionation/combination ratio is about 2; very similar values are obtained at 145 and 185 °C (Table II). We shall assume that this ratio is unaffected by the solvent isotope, i.e. that the ketyl radical does not distinguish between normal and deuteriated benzyl radicals to any significant extent. This allows us to perform the same analysis on the reaction of **1a** in normal toluene. For each temperature, b and c were estimated by minimizing the errors (least-squares treatment) in eq 3–6 to give the data in Table II. In all cases, b (hydrogen abstraction, process 4) is within 1–3% of the secondary alcohol yield and c (process 5) never accounts for more than 4% of the initially formed $Ad_2C^\bullet OH$.

This result means that hydrogen abstraction from the solvent is substantially faster than disproportionation of

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[7] As a result of new measurements on adamantane labeling (see Experimental Section) the cage effects are smaller than previously reported[8] and the disproportionation/combination ratios, consequently, higher.

[8] Lomas, J. S.; Briand, S. *Tetrahedron Lett.* **1989**, *30*, 707.

Table III. Thermolysis of Tri(1-adamantyl)methanol (Initially 6.25×10^{-3} M unless Stated) in Toluene: Product Simulation by Application of the Steady-State Assumption to the Intermediates, $S^{\bullet}$ and $Ad_2C^{\bullet}OH$

temp, °C	solv[a]	(a)	k_1, 10^{-4} s^{-1}	k_4, 10^1 s^{-1}	k_5, 10^8 M^{-1} s^{-1}	(k_6 + k_7),[b] 10^{10} M^{-1} s^{-1}	k_8, 10^{10} M^{-1} s^{-1}	(b + c + f)/2	(b)[c]	(c)[c]	(d + e)[c]
145	D	0.415	1.80	0.96	4.7	1.11	1.11	0.172 (0.172)	0.135 (0.135)	0.037 (0.037)	0.376 (0.378)
165	D	0.40	16.7	2.12	4.6	1.31	1.31	0.149 (0.149)	0.107 (0.107)	0.042 (0.042)	0.409 (0.409)
185	D	0.38	128.0	4.6	4.2	1.52	1.52	0.133 (0.133)	0.090 (0.090)	0.043 (0.043)	0.444 (0.444)
145	H	0.415	1.80	7.1	4.7	1.11	1.11	0.368 (0.368)	0.362 (0.346)	0.006 (0.021)	0.212 (0.196)
165	H	0.40	16.7	14.0	4.6	1.31	1.31	0.315 (0.317)	0.305 (0.315)	0.009 (0.000)	0.276 (0.291)
165	H[d]	0.40	16.7	14.0	4.6	1.31	1.31	0.353 (0.353)	0.347	0.006	0.241 (0.225)
165	H[e]	0.40	16.7	14.0	4.6	1.31	1.31	0.394 (0.377)	0.390	0.004	0.202 (0.192)
185	H	0.38	128.0	27.5	4.2	1.52	1.52	0.276 (0.278)	0.265 (0.265)	0.012 (0.010)	0.332 (0.334)

[a] D denotes toluene-d_8, H toluene-h_8. [b] ($k_6 + k_7$) taken arbitrarily equal to k_8; see text. [c] Target values given in parentheses. [d] [**1a**] = 3.10×10^{-3} M. [e] [**1a**] = 1.56×10^{-3} M.

ketyl radicals in normal toluene, while in deuteriated solvent a significant fraction of the secondary alcohol arises by this latter process. However, the complexity of the kinetic system is such that these figures still do not enable us to evaluate the isotope effect on hydrogen abstraction by the ketyl radical. This can only be achieved by kinetic modeling.

Kinetic Analysis and Product Simulation. The product composition is a reflection of the relative rates of the various processes occurring after the rate-determining step, and its dependence on the experimental conditions reveals how these rates depend on the concentration, temperature, and kinetic isotope effects. The only way of getting from the products to the rate constants, however, requires the construction of a plausible kinetic model into which trial rate constants must be injected until a good fit with experimental product data is obtained.

Insofar as the diffusion of radicals from the solvent cage will be much faster than the rate of their formation (constant k_1, see Scheme I), this latter will determine the rate of appearance of $Ad^{\bullet}$ and $Ad_2C^{\bullet}OH$ in solution. Given the high rate constant (as compared to that of thermolysis) for the reaction of the *tert*-butyl radical with toluene (14.4 M^{-1} s^{-1} at 48 °C[9]) and that $Ad^{\bullet}$ is probably of comparable reactivity,[10] we can reckon that $Ad^{\bullet}$ is immediately replaced by $S^{\bullet}$ and that, therefore, the rate of appearance of $S^{\bullet}$ is also governed by k_1. This assumption is supported by the observation that, apart from adamantane, insignificant amounts of products arising from the adamantyl radical are formed (see below).

The rate of formation of $S^{\bullet}$ is then given by:

$$d[S^{\bullet}]/dt = (1 - a)k_1[Ad_3COH] + k_4[Ad_2C^{\bullet}OH] - (k_6 + k_7)[Ad_2C^{\bullet}OH][S^{\bullet}] - 2k_8[S^{\bullet}]^2 \quad (7)$$

where k_4 includes the solvent concentration, [SL]. That of $Ad_2C^{\bullet}OH$ is:

$$d[Ad_2C^{\bullet}OH]/dt = (1 - a)k_1[Ad_3COH] - k_4[Ad_2C^{\bullet}OH] - 2k_5[Ad_2C^{\bullet}OH]^2 - (k_6 + k_7)[Ad_2C^{\bullet}OH][S^{\bullet}] \quad (8)$$

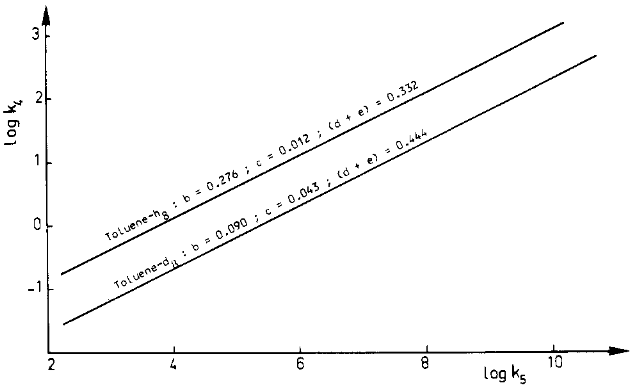

Figure 2. Product simulation: for a given $(k_6 + k_7)/k_4$ the value of k_5 depends on $(k_4)^2$ (T = 185 °C; $[\mathbf{1a}]_o = 6.25 \times 10^{-3}$ M; a = 0.38; $k_1 = 1.28 \times 10^{-2}$ s^{-1}; $(k_6 + k_7)/k_{4D} = 3.3 \times 10^8$ M^{-1}; $k_8 = 1.52 \times 10^{10}$ M^{-1} s^{-1}).

In the Appendix we show how these two equations can be put into a form whereby $[S^{\bullet}]$ can be calculated iteratively as the concentration of **1a** falls stepwisely from the initial value to zero; $[Ad_2C^{\bullet}OH]$ is also obtained, so the incremental contributions of each step to the final product concentrations may be evaluated and summed to give the fractional yields. The fixed points in the calculation are the initial concentration, the cage effect and the experimental rate constant for **1a** thermolysis, k_1.[2b] Values of k_8 were calculated by extrapolation of the Arrhenius plot of Fischer's data.[11] They are close to those obtained by averaging the toluene self-diffusion coefficients[12] (those from O'Reilly[12a] are 40–50% higher than those from Krüger[12b] in the temperature range considered) and applying the Smoluchowski equation.[11] It remains to assign values of k_4, k_5, and ($k_6 + k_7$). Trials showed, not unexpectedly, that for a given set of a (cage effect), ($b + c$) (secondary alcohol) and ($d + f$) (cross-product and disproportionation) there is an infinity of solutions. For a given $(k_6 + k_7)/k_4$ the same output can always be obtained with k_5 increasing as the square of ($k_6 + k_7$) or k_4, regardless of their absolute values (Figure 2). The easiest approach is to fit the data for the reaction in toluene-d_8 by trial and error, and then to increase k_4 until the new output matches the product data for the reaction in normal toluene. Because the values of the various components are calculated by a rather circuitous route and are very sensitive to small errors on the experimental data, the agreement is less good for the reaction in normal toluene (Table III). An idea of the precision of the relative rate constants is provided by the observation that a 10% change in k_4 results in a shift of about 0.01 in the major components.

For a reaction of lower concentrations of **1a** at 165 °C in toluene-h_8 the same set of rate constants predicts bibenzyl and secondary alcohol yields close to those found experimentally. Using the disproportionation/combination ratio of 2.0 to estimate ($d + e$) from the cross-product yield, we obtain values within 0.02 of those observed.

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[9] Dütsch, H. R.; Fischer, H. *Int. J. Chem. Kinet.* **1982**, *14*, 195.

[10] Engel, P. S.; Chae, W. K.; Baughman, S. A.; Marschke, G. E.; Lewis, E. S.; Timberlake, J. W.; Luedtke, A. E. *J. Am. Chem. Soc.* **1983**, *105*, 5030.

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The isotope effect on hydrogen abstraction from the solvent by the ketyl radical does not depend upon the choice of k_5, provided the same value is used for the calculations in the two solvents. It ranges from 6 at 185 °C to about 7.4 at 145 °C, rather large for such a high temperature and no doubt attributable to tunneling.[13] This appears to be a constant feature of hydrogen abstraction by radicals,[8,10] all of which have isotope effects substantially higher than the classical maximum.

Discussion

It is important to note that several compounds which might have been expected are absent (less than 1%) from the thermolysis product mixture. These include (1-adamantyl)toluenes, 1-benzyladamantane and 1,1′-biadamantyl, all of which are products of the photolysis of azo-1-adamantane in toluene.[10] This finding prompts several remarks. Firstly, side-chain hydrogen abstraction must be faster than ring attack under thermolysis conditions; this is an observation for which we have at present no explanation. Secondly, the absence of 1-benzyladamantane indicates that $S^\bullet$ and $Ad^\bullet$ do not coexist long enough to come together; $S^\bullet$ arises by reaction of $Ad^\bullet$ with the solvent in a relatively slow radical–molecule process, and then self-terminates or reacts with the ketyl radical in fast radical–radical processes. Finally, the absence of 1,1′-biadamantyl shows that $Ad^\bullet$ never reaches a sufficiently high concentration for self-termination to occur. This product is, of course, stable under our thermolysis conditions, cleaving only at much higher temperature.[14] Again, the absence of the possible cross-product, (1-adamantyl)diphenylmethanol,[15] **2b**, when BP is present, indicates that $BPH^\bullet$ and $Ad^\bullet$ do not react or, more probably, do not coexist. Once $Ad_2C^\bullet OH$ and $Ad^\bullet$ have escaped from the solvent cage, the system evolves as though the only reactive species were $BPH^\bullet$ and $S^\bullet$, the cross-product **2a** predominating.[16] It is remarkable that the yields of **2a** and bibenzyl are virtually unaffected by solvent deuteriation (Table I) even though process 3, hydrogen abstraction by $Ad^\bullet$, is much slower than in normal toluene.[8]

Analogous hydrogen transfers from a ketyl radical, generally hydroxyalkyl, to a carbonyl compound have been observed in both photochemically[17] and thermally induced[18–21] radical reactions. The thermolysis of **1a** with BP is closely analogous to the photochemical reduction of BP in toluene,[22] where the hydroxybenzhydryl radical is also an intermediate and where two of the principal products are bibenzyl and **2a**. However, as is usually observed in BP photoreduction,[17] benzpinacol is also found. It has been stated that disproportionation of hydroxybenzhydryl radicals is energetically unfavorable,[23] but this statement is certainly incorrect at higher temperature. The thermal decomposition of benzpinacol to benzophenone and benzhydrol has been studied kinetically in the range 80–141 °C in various solvents.[24] Benzhydrol rather than benzpinacol is formed in photoreductions at temperatures above 100 °C[25] and in the dialkyl peroxide induced reduction of benzophenone by secondary alcohols.[18] The analogous reduction of acetophenone, on the other hand, gives both phenylethanol and diphenylbutanediols,[18] evidently more stable than benzpinacol.

Since our product simulation gives only the relative values of k_4, k_5, and $(k_6 + k_7)$ based on an extrapolated k_8, the question of their absolute values is largely a matter of conjecture. Tertiary alkyl radicals with bulky substituents are often persistent, at least at room temperature and in inert solvents, while the di-*tert*-butylchloromethyl radical has a $2k$ of 10^5 M^{-1} s^{-1} at 223 K, decaying by first-order kinetics at higher temperature.[26] The 2-hydroxypropyl radical, on the other hand, has a $2k$ of about 10^9 M^{-1} s^{-1} at room temperature,[27] similar to that of the *tert*-butyl radical.[28] Data on relevant cross-reactions are just as scarce: benzyl couples with the 1-hydroxyethyl radical with $k = 2 \times 10^8$ M^{-1} s^{-1} at room temperature,[29] but there appear to be no data on its reactions with more encumbered radicals.

Our product data are incompatible with the assumption that the rate constants for all the radical–radical reactions are the same, though this is approximately true for the self and cross-reactions of small radicals,[9] nor can the rate of the cross-reaction be the geometric mean of those of the two self-reactions.[30] The simplest assumption (Table III) is that $(k_6 + k_7) = k_8$, whence we obtain values for k_4 of 0.7, 1.4, and 2.75 × 10^2 s^{-1} at 145, 165 and 185 °C, respectively. These lead to an entropy of activation of about −22.5 cal mol^{-1} K^{-1} and an enthalpy of activation of 11.8 kcal mol^{-1}. We calculate that at 48 °C k_4 is about 0.75 s^{-1}, which, after allowance for the toluene concentration, is some 200 times slower than benzylic hydrogen abstraction by the *tert*-butyl radical at this temperature ($k = 14.4$ M^{-1} s^{-1} in toluene [9]). This last statement obviously depends on the value assigned to $(k_6 + k_7)$; the enthalpy of activation will be the same whatever this is, while the entropy of activation rapidly becomes more negative as $(k_6 + k_7)$ falls (9 cal mol^{-1} K^{-1} for a factor of 10^2). Entropy data on hydrogen atom abstraction would enable us to situate k_4 approximately; even better would be direct measurements on one of these reactions.

Conclusion

The difference between $Ad_2C^\bullet OH$ and persistent tertiary radicals resides in the presence of a hydrogen atom which is readily transferred to an aryl ketone, to give a resonance stabilized ketyl radical, or to a benzyl radical. However, reactions with solvent molecules and self-termination are also important processes, involving hydrogen atom transfer to the encumbered carbon atom. The only possible manifestation of any steric effect upon its reactivity lies in the disproportionation/combination ratio for reaction with the benzyl radical, which is 3 times greater than that of the

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hydroxybenzhydryl radical, suggesting that the transition state for C–C bond formation is early, i.e. that it occurs when the two carbons are relatively distant and steric interactions are still small. A more direct approach to examining the question of steric effects on hydrogen abstraction or radical–radical reactions might be to study the reactivity of persistent radicals in hydrogen-donor solvents, but it is clear from the present work that alcohol thermolysis can provide useful semiquantitative information.

Experimental Section

Thermolysis. Aliquots (0.05 mL) of a solution of **1a** (usually 6.25×10^{-3} M) and benzophenone (0 to 6.25×10^{-3} M) in toluene-h_8 or toluene-d_8 (Aldrich 99+ %D) were sealed in Pyrex tubes under vacuum after 3–4 freeze–pump–thaw cycles. The dead space was about 0.2 mL. Batches of samples were thermostated at 145–185 °C for 10 half-lives. Product yields were determined by GC on packed SE30 columns, the detector response being calibrated by means of mixtures of authentic materials at concentrations similar to those obtained by thermolysis. In the absence of other detectable products, the sum of **1b**, **1c**, and **3** was assumed to represent 100%.[2b] Bibenzyl and **2a** were calibrated against **3**, and the relative yields were normalized. The tabulated data are averages of 2–6 samples and are reproducible to within 1%; i.e. 10% means 10 ± 1%. Absolute yields were determined by preparing solutions of **1a** and BP in a stock solution of dodecane and nonadecane (as internal standards for adamantane and Ad_2CO, respectively), thermolyzing as usual, and calibrating the GC response against solutions of pure AdH and ketone made up in the same stock.

Benzhydrol is poorly separated from benzophenone even on capillary GC. A solution of **1a** (55 mg) and BP (22 mg) in toluene (20 mL) was treated as above; the solvent was carefully removed by pumping at room temperature, and the ^1H NMR spectrum determined in $CDCl_3$. Comparison of the very small bibenzyl, **2a**, and benzhydrol signals at 2.92, 3.64, and 5.84 ppm, respectively, indicated a benzhydrol yield of 3–4% relative to **1a**.

1,1,2-Triphenylethanol (2a). By addition of benzylmagnesium bromide to benzophenone in ether: mp 89–90 °C (lit.[31] mp 91 °C); NMR ($CDCl_3$) δ 3.64 (s, 2 H), 6.8–7.5 (m, 15 H).

1,1-Di(1-adamantyl)-2-phenylethanol (1c). A solution of di(1-adamantyl) ketone, **3** (0.15 g, 0.5 mmol), and bromobenzene (1.8 g, 11 mmol) in dry ether (15 mL) was run slowly (15 mn) onto finely chopped lithium metal (0.42 g, 0.06 g-atom) magnetically stirred in ether (10 mL) under argon at −20 °C. The reaction mixture was maintained at −20 °C for 30 min and then allowed to warm slowly to room temperature. The crude product (after quenching in water, ether extraction, drying over $MgSO_4$, and removal of the solvent) was chromatographed in petroleum ether/ether mixtures. The product was recrystallized from benzene to give 0.16 g (81%): mp 217–8 °C NMR ($CDCl_3$) δ 1.65 and 1.97 (m, 30 H), 2.95 (s, 2 H), 7.1–7.4 (m, 5 H). Anal. Calcd for $C_{28}H_{38}O$: C, 86.10; H, 9.81. Found: C, 85.91; H, 9.74.

Deuterium Determinations. Products were separated on capillary GC (CP-Sil 5) and analyzed on a Finnigan MAT ITD 800B (ITD = ion trap detector) apparatus with electron ionization. Under these conditions the base peak of adamantane derivatives is at *m/e* 135 and the highest mass peak of alcohols is at *m/e* M − 17 or M − 135.

(i) Adamantane. Adamantane-*1-d* (98% as determined by conventional MS at 13 eV) was synthesized by Kuivila's method.[32] In a preliminary publication[8] we applied Engel's method[10] for the MS determination of adamantane labeling, assuming that the fragmentation of the ITD was analogous to that in MS and using the *m/e* 137/136 ratio to calculate the % AdH. Unfortunately, subsequent experiments showed that whereas the MS of AdD has no peak (less than 1%) at M − 2, under ITD conditions it is of the order of 4%. There is therefore a peak arising from AdD, which is confused with the M − 1 peak of AdH, enhancing the apparent AdH content. It was found necessary to use AdD–AdH mixtures to calibrate the ITD response in terms of the *m/e* 137/136 ratio. This gives a shallow curve at high AdH content (reproducibility ±3%), steepening toward high AdD content (±1–2%). Results (% AdH) in toluene-d_8 were (T (°C), no BP, with BP): 145, 41.5, 41.5; 165, 40.0, 40.5; 185, 38.0, 37.5.

(ii) Di(1-adamantyl)methanol (1b). Secondary alcohol labeled on the C–OH carbon was synthesized by $LiAlD_4$ reduction of the ketone. It was easily distinguished from Ad_2CHOH by the presence of two peaks at *m/e* 165 and 166 (M − 136 and M − 135), whereas the latter has the corresponding peaks at 164 and 165. The ITD response at *m/e* 164 and 166 was calibrated by means of mixtures of the alcohols at concentrations similar to those found in the thermolysis samples. Our measurements were checked on a Finnigan MAT 44S of the University of Freiburg: with chemical ionization the base peaks of the nonlabeled and labeled alcohols were M − 17 at *m/e* 283 and 284, and the H content was 18, 27, and 31% at 145, 165, and 185 °C, respectively, in reasonable agreement with our values of 25, 29, and 34%. Mean values are used in Table II.

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Appendix

Iterative Procedure for the Solution of Differential Equations. If we make the steady-state assumption for both intermediates, the right hand sides of eq 7 and 8 can be set to zero. For simplicity we shall write $A^\bullet$ for $Ad_2C^\bullet OH$, **1a** for Ad_3COH, and B for $(1 - a)$:

$$d[S^\bullet]/dt = 0 = Bk_1[\mathbf{1a}] + k_4[A^\bullet] - (k_6 + k_7)[A^\bullet][S^\bullet] - 2k_8[S^\bullet]^2 \quad (9)$$

$$d[A^\bullet]/dt = 0 = Bk_1[\mathbf{1a}] - k_4[A^\bullet] - 2k_5[A^\bullet]^2 - (k_6 + k_7)[A^\bullet][S^\bullet] \quad (10)$$

If $[S^\bullet]$ is set to zero in eq 10 we have a quadratic equation which can be solved for $[A^\bullet]$. If this value is put into eq 9 we have a quadratic equation which can be solved for $[S^\bullet]$, and so on, which means that both $[A^\bullet]$ and $[S^\bullet]$ can be calculated from any set of B, $[\mathbf{1a}]$, and the six rate constants. All that remains is to derive the yields of the various products from the calculated instantaneous values. Consider the case of the secondary alcohol, X, formed by hydrogen transfer from solvent to $A^\bullet$:

$$\frac{d[X]}{-d[\mathbf{1a}]} = \frac{d[X]/dt}{-d[\mathbf{1a}]/dt} = \frac{k_4[A^\bullet]}{k_1[\mathbf{1a}]}$$

Suppose that $\Delta C = [\mathbf{1a}]_o/n$ and replace $d[X]/-d[\mathbf{1a}]$ by $[\Delta X]_i/\Delta C$, where the initial alcohol concentration is divided into n increments and $[\Delta X]_i$ is the secondary alcohol contribution associated with the ith increment. Then:

$$[\Delta X]_i = \frac{k_4[A^\bullet]_i}{k_1[\mathbf{1a}]_i}(\Delta C)$$

where $[A^\bullet]_i$ and $[\mathbf{1a}]_i$ are the concentrations of $A^\bullet$ and **1a** at the ith step. The total concentration of X summed over all steps is then:

$$[X] = \sum_{i=1}^{n} \frac{k_4[A^\bullet]_i}{k_1[\mathbf{1a}]_i}(\Delta C)$$

The fractional yield of X is, finally:

$$[X]/[\mathbf{1a}]_o = \frac{1}{n} \sum \frac{k_4[A^\bullet]_i}{k_1[\mathbf{1a}]_i}$$

The integration process consists, therefore, in calculating

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for all values of i from 1 to n (where n is conveniently 1000) the corresponding concentrations of $S^\bullet$ and $A^\bullet$ ([$S^\bullet$] being iterated to any required degree of precision, 0.001% in our calculations) and summing the appropriate expressions for the rates of formation of the various products. Depending slightly on the relative values of the rate constants, each calculation takes a few seconds on a Digital VAX 6210.

Registry No. **1a**, 93754-90-6; **1b** (R = H), 54821-21-5; **1c**, 98395-36-9; **2a**, 4428-13-1; **4b**, 121862-05-3; Ad$^\bullet$, 2819-03-6; D_2, 7782-39-0; Ph_2CO, 119-61-9.

Mechanism of the Thermal Decomposition of Substituted Tetraoxanes in Benzene Solution: Effect of Substituents on the Activation Parameters of the Unimolecular Reactions

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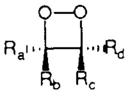
The kinetics and mechanism of the thermal decomposition reactions of three substituted tetraoxanes (benzophenone diperoxide, cyclohexanone diperoxide, and pinacolone diperoxide in benzene solution were investigated in the temperature range 108–165 °C. The activation parameters for unimolecular reactions of molecules of this type are interpreted in terms of substituent effects in the tetraoxacyclohexane ring. Isokinetic relationships are established which characterize a valid "reaction series" for the unimolecular thermolysis reactions of the substances considered, except for the acetone diperoxide homolysis. A general reaction mechanism for the thermolysis of the diperoxides is presented.

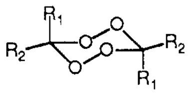
The thermolysis of dioxetanes of the general formula I where R_a, R_b, R_c, and R_d are aliphatic, alicyclic, polycyclic, or aromatic substituents have been the subject of intense mechanistic studies.[1] For example, it has been found that



I

the substitution in a series of 3,3-disubstituted 1,2-dioxetanes yields a systematic increase of less than 1 kcal mol^{-1} per alkyl group in the activation energies of their unimolecular decomposition reactions[2,3] and the replacement of a methyl by a phenyl group makes no change whatever in the respective activation parameters.[4] However, the introduction of 3,4-cyclic substituents produces larger effects on the thermolysis activation parameters.[5]

For some substituted tetraoxanes (ACDP–APDP–BKDP) the experimental evidence indicates thermal decomposition initiated by the formation of biradicals and not through concerted processes.[6–8] However, the thermolyses are complicated in certain cases (ACDP and BKDP) by induced decomposition reactions. It must be noted that the diperoxides APDP and PDP, with different R_1 and R_2 substituents, can exist in either cis and trans configurations, but in the former case the trans isomer is more stable.[9]



ACDP: $R_1 = R_2 = CH_3$
APDP: $R_1 = CH_3$; $R_2 = C_6H_5$
BKDP: $R_1 = R_2 = C_6H_5CH_2$
BPDP: $R_1 = R_2 = C_6H_5$
CHDP: $R_1{-}R_2 = -(CH_2)_5-$
PDP: $R_1 = CH_3$; $R_2 = t\text{-}C_4H_9$

Table I. Rate Constant Values for the Thermolyses of Substituted Tetraoxanes in Benzene Solution

diperoxide	temp, °C	10^3m, mol kg^{-1}	10^5k_{exp}, s^{-1}	10^5k_o,[a] s^{-1}
BPDP	130.7	17.2	0.26	0.26
	140.2	8.37	0.63	0.63
	150.3	9.54	1.61	
		18.6	1.63	1.62
	160.0	9.48	6.55	6.55
	165.5	6.23	8.54	8.54
CHDP	108.0	55	0.17	0.17
	120.5	40	0.76	0.76
	135.0	41	2.30	2.30
	150.0	55	22.0	22.0
	160.0	23	33.4	
		41	39.5	
		55	35.7	
		121	34.2	35.7 ± 2.3
PDP	120.0	15.2	3.57	
		92.4	3.40	3.49 ± 0.09
	140.0	7.1	25.1	
		15.2	28.8	
		170	28.3	27.4 ± 1.6
	160.0	7.1	135	
		170	125	130 ± 5

[a] Errors as standard deviations.

In this work we report the kinetics and mechanism of the thermal decomposition reactions in benzene solution of three substituted tetraoxanes (BPDP, CHDP, PDP) for comparison of their activation parameters with those corresponding to the unimolecular homolyses of the diperoxides ACDP, APDP, and BKDP.[6–8]

Results and Discussion

The thermal decomposition reactions of BPDP, CHDP, and PDP in benzene solution in the temperature and initial

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