JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 9, 507–513 (1996)

MECHANISM OF RuO_4-MEDIATED OXIDATIONS OF SATURATED HYDROCARBONS, ISOTOPE EFFECTS, SOLVENT EFFECTS AND SUBSTITUENT EFFECTS.

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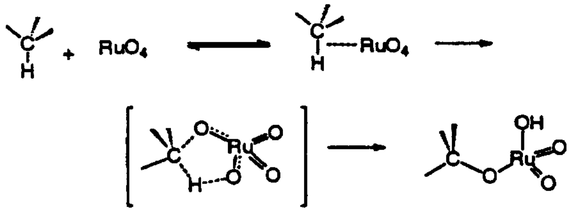
Adamantane and 1,3,5,7-tetradeuterioadamantane were oxidized by RuO_4 in two solvent systems, CCl_4–CH_3CN–H_2O and acetone–water, yielding two kinetic deuterium isotope effects (KIEs), 4·8 ± 0·2 and 7·8 ± 0·1, respectively, very similar to those obtained in analogous reactions with *cis*-decalin and perdeuterio-*cis*-decalin, 4·8 and 6·8. These results were interpreted as primary KIEs and small or negligible secondary KIEs. From this, sp^2-hybridized intermediates were not involved in the reaction path. The kinetic effect of the solvent was investigated by performing the reaction in aqueous acetone and acetonitrile. The rates were correlated with Grunwald–Winstein Y values and with Reichardt $E_T(30)$ values. Both correlations showed the reaction to be only moderately dependent on the solvent polarity. 1-Substituted adamantanes were oxidized in CCl_4–CH_3CN giving a Taft ρ^* value of $-2{\cdot}5 \pm 0{\cdot}1$. These results were regarded as support for a reaction consisting of a pre-equilibrium with formation of a substrate–RuO_4 complex followed by a rate-determining concerted reaction.



The results did not support a reaction mechanism with a carbocation or radical intermediate, or a scheme with two competing reactions, one with a carbocation intermediate and the other with a concerted mechanism.

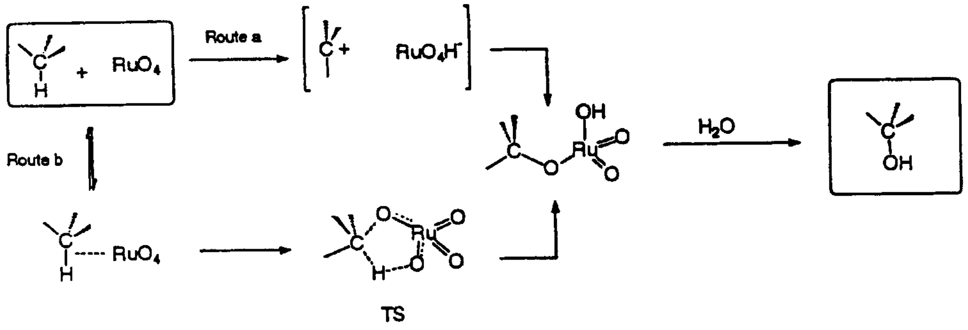
INTRODUCTION

We have recently reported the results from an investigation of the reaction mechanism of the RuO_4-mediated oxidation of saturated hydrocarbons. Two reaction pathways seemed possible from that study, either hydride abstraction and formation of an intimate ion pair (route a, Scheme 1), or by a pre-equilibrium with a hydrocarbon–RuO_4 complex followed by a concerted rate-determining step (route b).[1] Waegell and coworkers[2,3] have proposed a concerted mechanism for this oxidation reaction. Our proposal of a reaction mechanism was based on, among other results, the kinetic deuterium isotope effect (KIE) from the rates of oxidation of *cis*-decalin and perdeuterio-*cis*-decalin.[4] This observed KIE (4·8) might have been a product of a primary and a secondary KIE as the C-9 atom oxidized had five β-hydrogen/deuterium atoms. For a reaction with a carbocation or a radical intermediate, we would expect a substantial part of the observed KIE to be a secondary KIE and the primary KIE only a portion of it.[4]

The magnitude of the primary KIE contains important information on the reaction mechanism. We therefore considered it of some importance to have a reliable assessment of this quantity. This would also give an estimate of a possible secondary KIE. We have now determined the primary KIE of this oxidation. We have also investigated the solvent effect on the magnitude of the KIE. In addition, we report solvent effects on the Taft ρ^* values obtained from the oxidation of substituted adamantanes.

CCC 0894–3230/96/070507–07

Received 1 September 1995
Revised 26 February 1996



Scheme 1.

RESULTS

Kinetic deuterium isotope effect (KIE)

We first attempted to prepare 9,10-dideuterio-*cis*-decalin for an assessment of the primary KIE. This compound would have only one β-deuterium atom compared with five for perdeuterio-*cis*-decalin used in the previous investigation. However, it is known that hydrogenation of 1,2,3,4,5,6,7,8-octahydronaphtalene [$\Delta^{9(10)}$-octalin] by Pt catalysis produces *trans*-decalin.[5] We therefore tried to reduce $\Delta^{9(10)}$-octalin with diimide. However, no reduction took place and we decided to use 1,3,5,7-tetradeuterioadamantane (AdD_4) for the determination of the primary KIE. For AdH_4/AdD_4 only a primary KIE is possible.[6,7] The rates of oxidation of AdH_4 and AdD_4 in acetone–water and in CCl_4–CH_3CN–H_2O are given in Table 1.

1-Adamantanol (AdOH) and 2-adamantanone (Adon) were the only products from the RuO_4 oxidation of AdH_4. In acetone–water (3 : 1) we found these two compounds to be produced in a AdOH : Adon ratio of 97 : 3 for AdH_4 and 71 : 29 for the oxidation of AdD_4. These ratios were constant during the reaction (over three half-lives). The formation of both AdOH and Adon was first order in substrate. The observed product ratios therefore show the ratio of the pseudo-first-order rate constants k_{OH} and k_{on} (k_{OH} for the formation of AdOH and k_{on} for the formation of Adon). From this and k_{obs}, we obtain rate constants $k^{\mathrm{H}}_{\mathrm{OH}} = (0{\cdot}68 \pm 0{\cdot}02) \times 10^{-4}\ \mathrm{s}^{-1}$ and $k^{\mathrm{D}}_{\mathrm{OH}} = (0{\cdot}087 \pm 0{\cdot}005) \times 10^{-4}\ \mathrm{s}^{-1}$ ($k^{\mathrm{H}}_{\mathrm{OH}}$ for the oxidation of AdH_4 and $k^{\mathrm{D}}_{\mathrm{OH}}$ for AdD_4) and a $\mathrm{KIE} = k^{\mathrm{H}}_{\mathrm{OH}}/k^{\mathrm{D}}_{\mathrm{OH}} = 7{\cdot}8 \pm 0{\cdot}1$ in acetone–water.

For the oxidation of AdH_4 in CCl_4–CH_3CN a [AdOH] : [Adon] ratio of 99 : 1 and for AdD_4 92 : 8 were found. These figures then give $k^{\mathrm{H}}_{\mathrm{OH}} = (0{\cdot}2236 \pm 0{\cdot}0006) \times 10^{-4}\ \mathrm{s}^{-1}$, $k^{\mathrm{D}}_{\mathrm{OH}} = (0{\cdot}046 \pm 0{\cdot}002) \times 10^{-4}\ \mathrm{s}^{-1}$ and $\mathrm{KIE} = 4{\cdot}8 \pm 0{\cdot}2$.

From the relative rates of oxidation of *cis*-decalin and perdeuterio-*cis*-decalin in acetone–water (Table 2), a KIE of 6·8 ± 0·4 was found.

Table 1. RuO_4 oxidation of adamantane (AdH_4) and 1,3,5,7-tetradeuterioadamantane (AdD_4) in CCl_4–CH_3CN–H_2O (2 : 1 : 2), (solvent system A) at 30 °C, $[RH]_0 = 40$ mM, $[RuO_4] = 18{\cdot}4$ mM, and in acetone–water (3 : 1), (solvent system B) at 30 °C, $[RH]_0 = 25$ mM, $[RuO_4] = 4{\cdot}6$ mM

Substrate	Solvent system	$k_{\mathrm{obs}}/10^{-4}\ \mathrm{s}^{-1}$	Correlation coefficient, r^2
AdH_4	A	0·2259 ± 0·0006	0·99995
AdD_4	A	0·050 ± 0·002	0·987
AdH_4	B	0·70 ± 0·03	0·990
		0·70 ± 0·02	0·996
		0·71 ± 0·02	0·996
		0·69 ± 0·02	0·995
AdD_4	B	0·132 ± 0·002	0·997
		0·113 ± 0·002	0·996

Table 2. RuO_4-mediated oxidations of *cis*-decalin and perdeuterio-*cis*-decalin in acetone–water (3:1) at 30 °C, $[RH]_0 = 25$ mM, $[RuO_4] = 4{\cdot}6$ mM

Substrate	$k_{obs}/10^{-4}\ s^{-1}$	r^2
cis-Decalin	0·423 ± 0·004	0·9991
	0·426 ± 0·004	0·9993
$[^2H_{18}]$-*cis*-Decalin	0·058 ± 0·001	0·9964
	0·0663 ± 0·0008	0·9983

The KIEs obtained for the RuO_4 oxidations of adamantane and *cis*-decalin in two different solvent systems are given in Table 3.

No solvent deuterium isotope effects were observed from oxidation of *cis*-decalin in acetone–water and acetone–D_2O (see Table 5). No incorporation of deuterium in either substrate or product was found (0·1% would have been detected by gas chromatography–mass spectrometry (GC–MS)).

Substituent effects

We have reported the oxidation of 1-substituted adamantanes in acetone–water and the correlation of their reaction rates with the Taft's substituent constants σ^* to give the reaction constant σ^*.[1] From the large difference in the KIEs in the two solvent systems (Table 3), the reaction mechanism might be different in the two cases. We therefore oxidized these compounds in CCl_4–CH_3CN–H_2O (Table 4). Correlation of the reaction rates with Taft's σ^* values gave $\rho^* = -2{\cdot}0 \pm 0{\cdot}2$ or $-2{\cdot}5 \pm 0{\cdot}1$ if the results from AdH_4 ('substituent' = H) were omitted, as suggested by Schleyer and Woodworth.[8] The corresponding values obtained in acetone–water were $-1{\cdot}7 \pm 0{\cdot}1$ and $-2{\cdot}08 \pm 0{\cdot}03$, respectively.[1]

Solvent effects

In the previous investigation, we obtained an *m* value of 0·31 from the correlation of the reaction rates with the *Y* values in the Grunwald–Winstein equation.[1] Another method for assessment of solvent effects has been developed by Reichardt.[9] The solvatochromatic effect was used for solvent characterization and the E_T^N values determined for a number of solvents and solvent mixtures.

Table 4. RuO_4-mediated oxidation of 1-substituted adamantanes in CCl_4–CH_3CN–H_2O (2:1:2) at 30 °C, $[RH]_0 = 40$ mM, $[RuO_4] = 20{\cdot}7$ mM[a]

Substituent	$k_{obs}/10^{-6}\ s^{-1}$	r	σ^{*b}
H	25·6 ± 0·1	0·99996	0
OH	7·5 ± 0·1	0·9986	0·56
	7·0 ± 0·2	0·997	
NHAc	6·7 ± 0·2	0·997	0·58
	6·7 ± 0·2	0·993	
Cl	0·4 ± 0·1	0·70	1·02
	0·37 ± 0·04	0·940	
Br	0·58 ± 0·06	0·948	0·98
	0·87 ± 0·08	0·952	
CN	0·3 ± 0·2	0·35	1·24
	0·10 ± 0·05	0·49	

[a] $\rho^* = \sigma^*/\log(k/k_0) = -2{\cdot}0 \pm 0{\cdot}2$ including H as a substituent. $\rho^* = -2{\cdot}5 \pm 0{\cdot}1$ excluding H as a substituent.
[b] Ref. 23.

The rates of reaction of *cis*-decalin in a few other one-phase solvent systems are given in Table 5 together with the E_T^N values. These were determined for only a few of the solvent mixtures that can be used together with RuO_4. For the other solvent mixtures, the E_T^N values of the neat organic solvent are presented to give a qualitative estimation of the solvent polarity.[10]

The rates of oxidation of *cis*-decalin in acetone–water and acetonitrile–water mixtures were correlated with the $E_T(30)$ values of these mixtures[11] (Figure 1). For the oxidation in acetone–water a rate gradient of 0·17 ± 0·04 was obtained. For acetonitrile–water, only two different compositions could be used as *cis*-decalin was not soluble in more water-rich mixtures. For this system a gradient of 0·28 was obtained.

Table 3. Kinetic deuterium isotope effects (KIEs) for the RuO_4-mediated oxidation of alkanes

Substrate system	Solvent	KIE
AdH_4/AdD_4	CCl_4–CH_3CN–H_2O	4·8 ± 0·2
cis-Decalin/perdeuteriated-*cis*-decalin	CCl_4–CH_3CN–H_2O	4·8[a]
AdH_4/AdD_4	Acetone–water (3:1)	7·8 ± 0·1
cis-Decalin/perdeuteriated-*cis*-decalin	Acetone–water (3:1)	6·8 ± 0·4

[a] Ref. 4.

Table 5. RuO_4-mediated oxidation of *cis*-decalin in various solvent systems at 30 °C, $[RH]_0 = 13$ mM, $[RuO_4] = 2{\cdot}88$ mM

Solvent system	k_2 10^{-4} s^{-1}	r^2	Y_{Tos}	$E_T(30)$[c]	E_T^N of neat organic solvent[d]
$CH_3COOH-H_2O$ (3 : 1)[a]	62 ± 2	0·996	—	—	0·648
	65·1 ± 0·3	0·9997			
CH_3CN-H_2O (3 : 1)	121 ± 3	0·991	—	55·59	0·460
CH_3CN-H_2O (2·3 : 1)[b]	159 ± 7	0·990	—	55·99	
	155 ± 2	0·9996			
DMF–H_2O (3 : 1)	no reaction	—	—	—	0·386
Acetone–D_2O (3 : 1)	142 ± 3	0·997			
	155 ± 7	0·991			
Acetone–H_2O (3 : 1)	149 ± 7		−0·50	51·81	0·355
Acetone–H_2O (2·3 : 1)	211 ± 1		0·07	52·50	
Acetone–H_2O (1·5 : 1)	338 ± 25		0·66	53·08	
Acetone–H_2O (1·3 : 1)	396 ± 3		0·91	54·31	

[a] $[RH]_0 = 6{\cdot}5$ mM, $[RuO_4] = 3{\cdot}6$ mM.
[b] $[RH]_0 = 6{\cdot}5$ mM, $[RuO_4] = 2{\cdot}88$ mM.
[c] Ref. 10.
[d] Ref. 11.

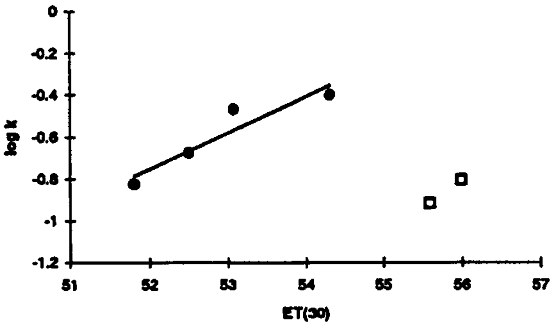


Figure 1. Correlation of reaction rates with $E_T(30)$ values for RuO_4-mediated oxidations of *cis*-decalin in (●) acetone–water and (☐) acetonitrile–water mixtures

DISCUSSION

Kinetic deuterium isotope effect (KIE)

From the rates of reaction of *cis*-decalin and perdeuterio-*cis*-decalin in CCl_4-CH_3CN, a KIE of 4·8 was found.[4] This may have had a contribution from a secondary KIE due to five deuterium atoms β to the reacting C-9 atom. From the rates of oxidation of AdH_4 and AdD_4 we were able to calculate a primary KIE without any contributions from a secondary KIE.

We obtained the same KIE, perhaps fortuitous, from the oxidation of AdH_4/AdD_4 in $CCl_4-CH_3CN-H_2O$ as that obtained from *cis*-decalin/perdeuterio-*cis*-decalin (KIE = 4·8). In acetone–water, the KIEs for both sets of compounds were larger (Table 3). These figures might include some tunnelling effects. However, the variable-temperature experiments reported earlier indicated that any tunnelling effect would be fairly small.[4] We have not investigated this point any further.

If a carbocation were formed at C-9 in the oxidation of perdeuterio-*cis*-decalin (route a in Scheme 1) the carbocation would have five β-deuterium atoms. The conformation of this carbocation has been discussed,[12] and from this and from inspection of models it is clear that the empty p-orbital of the cation would be almost parallel with three β C – D bonds. This is the most favourable configuration for a β secondary KIE and a KIE of 1·1–1·2 per deuterium atom would have been expected.[6] If a carbocation was formed, we would therefore have anticipated a substantial secondary KIE. As the observed KIEs obtained from the oxidations of adamantane and *cis*-decalin were the same for the reaction in CCl_4-CH_3CN and almost the same in acetone–water ($KIE_{decalin}/KIE_{adamantane} = 0{\cdot}8$) we conclude that the reaction did not involve an intermediate with an sp^2-hybridized C-9. The substantial primary KIE observed shows that a C – H bond was broken in the rate-determining step.

A pronounced solvent dependence of the KIE was observed for both substrates, with an increase in the KIE on going from CCl_4-CH_3CN to acetone–water. The solvent and substituent effects (see below) on the rate of oxidation indicated the reaction to have a polar transition state. This would be better stabilized in polar media, presumably with a more symmetric bond breaking/bond formation resulting in a larger KIE than in non-polar media with a more unsymmetric TS. The oxidation in acetone–water showed an activation free energy slightly smaller than that in CCl_4-CH_3CN, 20 vs 22 kcal mol^{-1} (1 kcal = 4·184 kJ) in accordance with this (Table 6).

Table 6. Activation parameters for the RuO_4-mediated oxidation of adamantane and *cis*-decalin in CCl_4–CH_3CN–H_2O (2 : 1 : 2), $T_{average}$ = 30·2 °C, and in acetone–water (3 : 1), temperature range 10–40 °C, $T_{average}$ = 32·4 °C

Substrate	Solvent	$\Delta H^{\ddagger}$/kcal K^{-1} mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}	$\Delta G^{\ddagger}$/kcal K^{-1} mol^{-1}
Adamantane	CCl_4–CH_3CN–H_2O	14·8 ± 0·6	−24·6	22·3
	Acetone–water	14·0 ± 0·3	−20 ± 1	20·1
cis-Decalin	CCl_4–CH_3CN–H_2O	14·7 ± 0·4	−26·2	22·6
	Acetone–water	12·3 ± 0·7	−26 ± 2	20·2

The opposite solvent effect, an increase in KIE on changing to less polar solvents, has been explained within the framework of tunnelling theory.[13] We observed an increase in the KIEs on going to more polar solvents and the reason for this therefore cannot be tunnelling effects.

Substituent effects

From the oxidation of 1-substituted adamantanes, negative ρ^* values were observed in CCl_4–CH_3CN (−2·5) and also in acetone–water (−2·08) (Table 4). These values indicate a polar TS. For reactions with a carbocation intermediate more negative ρ^* values were observed, $\rho^* = -3{\cdot}1$ for the solvolysis of 3-substituted 1-adamantyl tosylates and −2·7 for the solvolysis of 1-adamantyl chloride.[14] Nevertheless, the observed ρ^* values are large, and larger than expected for a concerted reaction.

Solvent effects

In Scheme 1, two different reaction mechanisms were shown for the RuO_4 oxidation of alkanes. The polarity of the solvent would have different influences on the rate of reaction for these two routes. For route a via a carbocation, an increase in the polarity would lead to a large increase in the rate of reaction.[15] For route b, the influence of the polarity would be small or negligible. In addition to the polarity, several other properties of the solvent might be of importance, e.g. hydrogen bonding abilities and, in the present case, complexation of the solvent with the ruthenium species, both in the ground state and in the TS. Our main goal was to investigate the influence of the polarity of the solvents, but our results may also shed some light on the latter points.

A rate gradient of 0·17 ± 0·04 was obtained when the rates of reaction were correlated with Reichardt's $E_T(30)$ values. Solvolysis of tert-butyl chloride has been found to have a gradient of 0·312, while a presumably non-polar [4 + 2] cycloaddition had a gradient of 0·016.[16] The corresponding *m* value obtained from the Grunwald–Winstein equation (0·31) was within the range observed for S_N2 reactions (0·25–0·35) and smaller than that of S_N1 reactions (1·0).[17] These results indicate a polar TS for the reaction but not a carbocation intermediate.

Correlation of the rate of oxidation in acetone–water and in acetonitrile–water with $E_T(30)$ gave two separate curves (Figure 1), one for each of the two organic solvents. Although only two acetonitrile–water mixtures could be used, this nevertheless indicates that other solvent properties than the polarity have influence on the rate of reaction. The reaction mixtures showed UV spectra in acetone–water, acetonitrile–water and CCl_4–CH_3CN (both organic and aqueous phase) identical with those reported for RuO_4 in neat CCl_4 and water.[18] This shows that RuO_4 was the active oxidant in all cases and not any of the lower oxidation state ruthenium species. The activation parameters $\Delta H^{\ddagger}$ and $\Delta G^{\ddagger}$ are slightly lower in acetone–water than in CCl_4–CH_3CN–H_2O (Table 6).

Reaction mechanism

Previous results indicated that the RuO_4 oxidation of saturated hydrocarbons proceeds either by a hydride abstraction mechanism (route a, Scheme 1) or by a two-step reaction, a pre-equilibrium followed by a concerted but not synchronous rate-determining step (route b).[1] The results have also been explained by two competing reaction paths: a concerted reaction and one via a carbocation intermediate.[4] A radical reaction by a hydrogen atom abstraction would have to proceed by a rapid rebound reaction in a solvent cage as no chlorinated products were observed from the reactions in CCl_4–CH_3CN[1] and the oxidations of alkylcyclopropanes gave unrearranged products.[19] This reaction mechanism is not excluded, but the lifetime of the radical intermediate would have to be less than 10^{-8} s.[20]

From the present investigation we have the following

(i) the reaction shows a large primary KIE and no significant secondary KIE; the KIE was solvent dependent;
(ii) a rather large substituent effect was observed in both CCl_4–CH_3CN and acetone–water;
(iii) the polarity of the solvent had only a moderate influence on the rate of reaction.

A reaction via hydride abstraction and formation of an intimate ion pair (route a) seems less likely from the present results. The use of both the Grunwald–Winstein equation and Reichardt's solvent polarity parameters indicated that the solvent polarity had only a moderate influence on the rate of reaction. Furthermore, the absence of a significant secondary β-KIE is not in accordance with a reaction via a carbocation.

If a non-polar concerted mechanism and a carbocation mechanism were competing,[4] all the observed effects would be a weighted average for the two competing reactions. Changing the solvent or the substrate would produce changes in the observed effects. We would expect the carbocation route to be more important in the more polar medium of acetone–water and therefore that the substituent effects would be larger for reactions run in this medium. However, the substituent effects were slightly larger in the less polar CCl_4–CH_3CN solvent than in acetone–water, contrary to this. Furthermore, point (i) indicated that carbocation intermediates were not important in either polar or non-polar media. Finally, nucleophiles were not incorporated into the products in the acetone–water medium.[1]

Route b with a pre-equilibrium and a subsequent concerted rate-determining step with a polar TS would explain the evidence outlined above. This mechanism would show a primary KIE because a C – H bond is broken in the rate-determining step [point (i)]. The primary KIE could be larger in acetone–water owing to a more symmetrical TS. The reaction would have no, or only a small, secondary KIE. The strength of the complex between RuO_4 and the C – H bond would depend on the electron density of the C – H bond and thus on the substituents in the vicinity of the carbon atom [point (ii)]. The polarity of the reaction medium would not be important as no carbocation is formed during the reaction [point (iii)]. This model would also explain the sensitivity to steric hindrance and the lack of rearrangements and inversion of configuration observed.[2–4]

CONCLUSION

The evidence presented above is in accordance with a two-step reaction mechanism for the RuO_4-mediated oxidation of saturated hydrocarbons:[1] the first step a pre-equilibrium and the second a concerted rate-determining one. Both a one-step hydrid abstraction reaction mechanism and a one-step concerted mechanism appear to be excluded by the results.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 FT NMR system. Mass spectra were recorded on a AEI MS 902 double-focusing high-resolution instrument. Melting points were measured on a Büchi melting point apparatus (not corrected). GC–MS was carried out on a Fision Instrument Trio 1000 GC–MS system equipped with a 25 m BP-1 fused-silica capillary column.

The methods used for the kinetic investigations and the analysis have been reported.[1,4] In all kinetic experiments, k_{obs} values were determined from more than eight measurements.

1,3,5,7-Tetrabromoadamantane was prepared using the method of Solott and Gilbert.[21] The product was 97% pure (GC), 3% 1,3,5-tribromoadamantane, m.p. 244–245 °C (lit.[21] 245–247 °C). ^{1}H NMR (400 MHz, $CDCl_3$): 2·704 (s). ^{13}C NMR (100 MHz, $CDCl_3$): 54·59, 54·81. MS (170 °C, 70 eV): m/z (relative intensity, %) 456 (0·45), 455 (0·15), 454 (1·22), 453 (0·36), 452 (1·41), 451 (0·30), 450 (1·26), 449 (0·17), 448 (0·34), 376 (3), 375 (34), 374 (13), 373 (97), 372 (11), 371 (100), 370 (4), 369 (35), 329 (2), 327 (3), 293 (5), 291 (6), 131 (10), 130 (10), 92 (4), 91 (23), 65 (16), 64 (21), 44 (83).

1,3,5,7—Tetradeuterioadamantane was prepared by the method of Sunko *et al.*[22] The product was >99% pure (GC). ^{1}H NMR (400 MHz, $CDCl_3$): 1·731 (s). ^{13}C NMR (100 MHz, $CDCl_3$): 37·51 (s), 27·74 (t, $J_{CD} = 20$ *Hz). MS (140 °C, 70 eV):* m/z (relative intensity, %) 141 (1·4), 140 (8), 138 (1), 111 (1), 110 (3), 98 (6), 97 (26), 96 (4), 81 (4), 59 (4), 58 (7), 56 (5), 55 (4), 45 (83), 44 (100), 43 (21).

ACKNOWLEDGEMENT

The support from the Norwegian Research Council is gratefully acknowledged.

REFERENCES

1. J. M. Bakke and A. E. Frøhaug, *Acta Chem. Scand.* **48**, 160–164 (1994).
2. A. Tenaglia, E. Terranova and B. Waegell, *Tetrahedron Lett.* **30** 5271–5274 (1989); A. Tenaglia, E. Terranova and B. Waegell, *J. Chem. Soc., Chem. Commun.* 1344–1345 (1990); A Tenaglia, E. Terranova and B. Waegell, *J. Org. Chem.* **57**, 5523–5528 (1992).
3. J.-L. Coudret and B. Waegell, *Inorg. Chim. Acta* **222**, 115–122 (1994).
4. J. M. Bakke and D. Bethell, *Acta Chem. Scand.* **46**, 644–649 (1992).
5. R. P. Linstead, A. B.-L. Wang, J. H. Williams and K. D. Errington, *J. Chem. Soc.* 1136–1140 (1937); N. I. Schuikin, *Chem. Zentralbl.* **106**, 3650–3651 (1935).
6. D. E. Sunko and W. J. Hehre, *Progr. Phys. Org Chem.* **14**, 205–246 (1983).
7. L. Melander and W. H. Saunders, Jr, *Reaction Rates of Isotopic Molecules*, Chapt. 5. Wiley, New York (1980).
8. P. v. R. Schleyer and C. W. Woodworth, *J. Am. Chem. Soc.* **90**, 6528–6530 (1968).
9. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., Chapt. 7.4, VCH, Weinheim (1988).
10. C. Reichardt, *Chem. Rev.* **94**, 2319–2358 (1994).
11. T. M. Krygowski, P. K. Wrona, U. Zielkowska and C. Reichardt, *Tetrahedron* **41**, 4519–4527 (1985).
12. A. F. Boschung, M. Geisel and C. A. Grob, *Tetrahedron*

Lett. **50**, 5169–5172 (1968); K. B. Becker, A. F. Boschung, M. Geisel and C. A. Grob, *Helv. Chim. Acta* **56**, 2747–2759 (1973).

13. E. F. Caldin and S. Mateo, *J. Chem. Soc., Faraday Trans. 1* **71**, 1876–1904 (1975); N. Sugimoto, M. Sasaki and J. Osugi, *J. Phys. Chem.* **86**, 3418–3423 (1982).
14. C. A. Grob and B. Schaub, *Helv. Chim. Acta* **65**, 1720–1727 (1982).
15. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., Chapt. 5.3.1. VCH, Weinheim (1988).
16. C. Reichardt, *Pure Appl. Chem.* **54**, 1867–1884 (1982).
17. C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed., p. 353, VCH, Weinheim (1988).
18. D. G. Lee and M. van den Engh, in *Oxidations in Organic Chemistry, Part B*, edited by W. S. Trahanovsky, pp. 177–227, Academic Press, New York (1973).
19. T. Hasegawa, H. Niwa and K. Yamada, *Chem. Lett.* 1385–1386 (1985).
20. P. R. Oritz de Montellano and R. A. Stearns, *J. Am. Chem. Soc.* **109**, 3415–3420 (1987).
21. G. P. Solott and E. E. Gilbert, *J. Org. Chem.* **45**, 5405–5408 (1980).
22. D. E. Sunko, S. Hirsl–Starcevic, S. Pollack and W. J. Hehre, *J. Am. Chem. Soc.* **101**, 6163–6170 (1979).
23. R. W. Taft, Jr, in *Steric Effects in Organic Chemistry*, edited by M. S. Newman, p. 556, Wiley, New York (1956); R. W. Taft, Jr, and I. C. Lewis, *J. Am. Chem. Soc.* **80**, 2436 (1958).