Methyl-d_3 Isotope Effects, α-Methyl Hydrogen Rate Effects, and the Analysis of Some Solvolytic Reaction Mechanisms[1]

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Abstract: The previously published linear correlation between the logarithms of the rate effect of α-methyl substitution for α-H in carbonium ion reactions and the logarithms of the rate effect of α-methyl deuteration has been shown to apply to several new examples. Deviations from the correlation in the direction of larger α-CH_3/CD_3 effects for some solvolyses of 2-methyl-2-chloroadamantane have been shown to be caused by a contribution to the isotope effects from partial rate-determining elimination in the tight ion pair. The deviation already observed for 7-methylnorbornyl tosylate seems to have a similar cause, but the mechanistic picture is further complicated by the occurrence of elimination at both intimate and solvent-separated ion pair stages.

Substituent effects on reaction rates have long been used to aid in the interpretation of the mechanisms of reaction. It has long been known that replacing hydrogen on the reaction center by methyl leads to a "methyl effect" which increases the rate of carbonium ion type reactions by a factor up to 10^6.[3,4] This apparent electron-releasing ability of a methyl group relative to hydrogen has been attributed to both inductive and hyperconjugative interactions,[5] but the quantitative separation of these effects has proved difficult because of additional complicating factors such as steric interactions, solvation effects, etc.

A key reference point in the analysis of such effects would be the rate effect of replacing the α hydrogen of isopropyl by methyl. Unfortunately, isopropyl derivatives generally solvolyze by different mechanisms than do the *tert*-butyl analogs so that the observed rate ratios underestimate the methyl group effect. In order to minimize the effect of solvent nucleophilicity in accelerating the rate of isopropyl bromide relative to *tert*-butyl bromide, Streitwieser, using the data in formic acid, identified the rate ratio of 10^6 as the *minimum* which would apply to the stabilization of a tertiary carbonium ion relative to a secondary ion in limiting solvolyses.[4]

Until recently, all observed α-CH_3/H rate ratios were smaller than this estimated minimum.[6] However, in 1967, Tanida[7] reported the exceptionally high α-CH_3/H ratio of $10^{7.7}$ for acetolysis of 7-norbornyl tosylate and its 7-methyl derivative. Shortly afterward, Schleyer[8] found a similarly high rate ratio for the solvolysis of the 2-adamantyl bromides. The fact that the *tert*-butyl bromide/isopropyl bromide rate ratio was smaller than 10^8 was attributed by Schleyer[8] to solvent participation in the isopropyl bromide reaction, which was absent in the reaction of *tert*-butyl bromide and in both the secondary and tertiary 2-adamantyl derivatives.

In 1968, Servis, Borčić, and Sunko[9a] observed, for solvolyses of a number of compounds, a remarkably linear correlation between the logarithms of the α-CH_3/H rate ratios and the logarithms of the α-CH_3/CD_3 β-secondary isotope effects. This is shown in Figure 1 with the original points indicated by "+". This observation was taken as indicative of a common, mostly hyperconjugative origin of these two effects.[9b] One potential application of this correlation would be to use the readily and accurately obtainable α-CH_3/CD_3 ratios for the estimation of carbonium ion solvolysis rates for secondary substrates. Isotopic substitution induces only small changes in rates and mechanisms[10] compared with the gross effects caused by replacement of hydrogen by methyl. In most cases, the large α-CH_3/H rate ratios can only be obtained through extrapolation to different temperature, leaving groups, or solvent which is generally not very accurate.[9,11,12] Even then the possibility of a significant change in mechanism remains.

We have determined α-CH_3/CD_3 isotope effects for solvolysis of 7-methylnorbornyl tosylate[13] and found a significant deviation from the original linear plot[14] as indicated in the upper right-hand corner in Figure 1. Since it appears unlikely that this discrepancy could be due to a nucleophilic attack on the secondary system,[15,16] a more detailed investigation was deemed necessary. One obvious complicating factor requiring further analysis is the possible influence of a primary isotope effect in the rate-determining elimination on the observed α-CH_3/CD_3 rate ratio.[13,17-20] A detailed method for sorting out the contributions to the overall isotope effects from the different solvolytic steps has been published recently[20] and provides a basis for compensating for the effects of rate-determining elimination in this work.

Methods and Results

Three new secondary-tertiary pairs (**1, 3, 4**) and one new primary-secondary pair (**2**) of compounds were investigated to compare with those which were originally used as the basis for the Servis, Borčić, Sunko (SBS) correlation.[9] The synthetic procedures not previously published are described in the Experimental Section. The kinetic measurements were performed using published procedures.[21-23] The results are given in Tables I and II.

Discussion

α-CH_3/H and α-CH_3/CD_3 rate ratios derived from the data in Tables I and II and from some data in the literature are compiled in Table III. For each entry is indicated the observed ratio *and* the predicted α-CH_3/CD_3 ratio which was obtained from the observed α-CH_3/H ratios and the SBS correlation equation

$$\log (\alpha\text{-}CH_3/CD_3) = 0.02024 \log (\alpha\text{-}CH_3/H)$$

Entries for these compounds are shown as full dots in Figure 1.

It can be seen that a good agreement exists between the observed and the predicted values for the isotope effects for compounds **1** and **2**. In addition to the new results reported in Tables I and II, information already published[17,22] can be used to include a point for *p*-methyl-1-phenylethyl chlo-

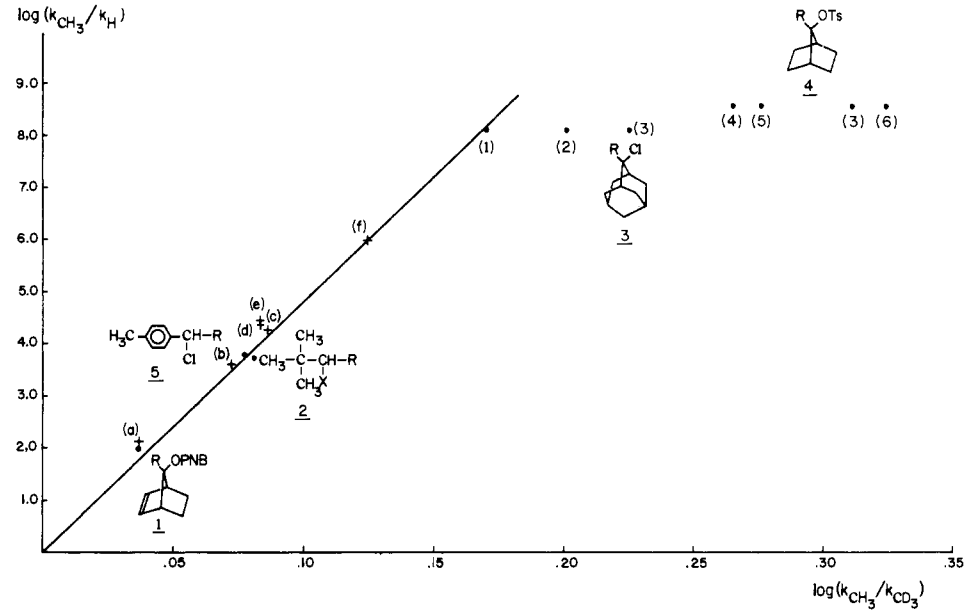
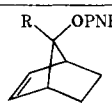
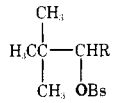


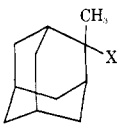
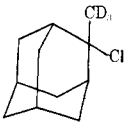
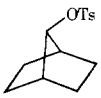
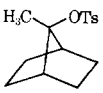
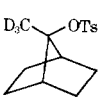
Figure 1. α-Methyl substituent effects *vs.* methyl-d_3 isotope effects: (a) cyclobutyl; (b) cyclopropylcarbinyl; (c) *exo*-2-norbornyl; (d) cyclohexyl; (e) cyclopentyl; (f) 2-propyl. All entries are for the corresponding chlorides.[9a] (1) 50 vol % ethanol; (2) 70 vol % ethanol, (3) 80 vol % ethanol; (4) acetic acid; (5) 97 wt % trifluoroethanol; (6) 80 wt % trifluoroethanol.

Table I. Solvolysis Rates for 7-Norbornenyl and Neopentyl Derivatives

Compd	Solvent[a]	Temp, °C	k, sec^{-1} R = H	k, sec^{-1} R = CH_3	k, sec^{-1} R = CD_3
1 	70 A[a]	25	5.85×10^{-12} [b]	5.90×10^{-10}	
	70 A[a]	110		5.90×10^{-5}	5.42×10^{-5}
2 	50 E	25	1.90×10^{-8}	1.008×10^{-4}	0.836×10^{-4}

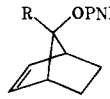
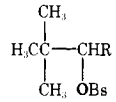
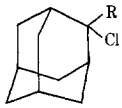
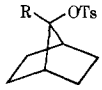
[a] 70 A is 70 vol % aqueousacetone; 50 E is 50 vol % ethanol. [b] Calculated from data in ref 24.

Table II. Solvolysis Rates and Products for 2-Adamantyl and 7-Norbornyl Derivatives

Compd		Solvent[a]	Temp, °C	k, sec^{-1}	Products % olefin	% alcohol	% ether
3b 	X = Cl	80 E	25	6.430×10^{-5}	33	43	23
		70 E	25	24.51×10^{-5}	25	57	18
		50 E	25	339.8×10^{-5}	7	84	8
	X = Br	80 E			21.5	51	27.5
		50 E			6.5	83.5	10
3c 		80 E	25	3.825×10^{-5}	19	57	24
		70 E	25	15.41×10^{-5}	10.5	71	18.5
		50 E	25	229.5×10^{-5}	2	88	10
4a 		AcOH[b]	25	6.36×10^{-5}			
4b 		AcOH	25[c]	2.50×10^{-6}			
			60	3.23×10^{-4}			
			70	1.08×10^{-3}	71[d]	29[d]	
		80 E	40	1.21×10^{-4}	65.4	22.7	11.8
		97 T	20	4.69×10^{-4}	62.4	5.6	32.0
		80 T	20	4.89×10^{-4}	51.4	28.7	19.9
4c 		AcOH	70	5.55×10^{-4}	51[d]	49[d]	
		80 E	40	0.66×10^{-4}	48.3	22.9	28.8
		97 T	20	2.22×10^{-4}	53.7	1.3	45.3
		80 T	20	2.44×10^{-4}	45.4	30.1	24.5

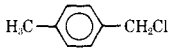
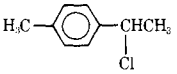
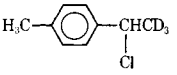
[a] E is vol % aqueous ethanol; T = wt % aqueous trifluoroethanol. [b] Reference 25. [c] Extrapolated from rates at higher temperatures; $\Delta H^{\ddagger}$ = 26.7 kcal/mol; $\Delta S^{\ddagger}$ = 5.5 eu. [d] Acetolysis products based on yields of alkene and acetate (listed on place of alcohol) at 75°, ref 12.

Table III. α-CH_3/H Rate Ratios and α-CH_3/CD_3 Rate Effects for *anti*-7-Norbornenyl, Pinacolyl, 2-Adamantyl, and 7-Norbornyl Derivatives

	Compd	k_{CH_3}/k_H		$(k_{CH_3}/k_{CD_3})_{obsd}$		(k_{CH_3}/k_{CD_3}) predict[a]
1		10^{2} [d]	(70 A)[c]	1.09	(70 A)[c]	1.09
2		$10^{3.73}$	(50 E)[c]	1.206	(50 E)[c]	1.206
3		$10^{8.12}$ [b]	(AcOH)	1.48 1.59 1.68	(50 E)[c] (70 E) (80 E)	1.45
4		$10^{8.6}$ [d]	(AcOH)	1.94 2.11 1.84 2.00	(AcOH) (97 T) (80 E) (80 T)	1.49

[a] From the SBS plot, ref 7. [b] For bromides in acetic acid, ref 6. [c] 70 A = 70 vol % aqueous acetone; 50 E = 50 vol % aqueous ethanol. [d] The rate for R = H taken from ref 24; see also ref 29.

Table IV. Solvolysis Rates for the *p*-Methylbenzyl and Benzyl Chlorides

	Compd	Solvent[a]	Temp, °C	$k \times 10^5$, sec^{-1}	Ref
5b		97 T	25	67.3	17
6a		97 T	25	0.644	17
6b		80 E	25	58.87	22
5b		80 E	25	1.002	22
5c		97 T 80 E	25 25	55.21 0.819	17 22
6c		80 E	25	49.10	22

[a] T = wt % aqueous trifluoroethanol; E = vol % aqueous ethanol.

ride (**6b**) in the correlation. The relevant data are given in Table IV. Assuming that the rate effect of the *p*-methyl group in *p*-methyl-1-phenylethyl chloride is the same in 97 T as in 80 E, one can use these data to calculate the rate effect of CH_3 *vs.* α-H substitution for the *p*-methyl compounds by multiplying the rate ratio of the first two compounds in Table IV (**5b** and **6a**) by that of the third and fourth entries (**6b** and **5b**). The resulting ratio is 6140. The isotope effect estimated for the *p*-methyl-1-phenylethyl-*2,2,2-d*$_3$ chloride (**6c**) in 97 T at 25° is 1.196.[26] This value corresponds to a value of 1.194 estimated from the SBS plot. It should also be pointed out that the rather detailed mechanistic analysis based principally on α-D isotope effects indicates that all of these compounds solvolyze under the conditions indicated, with the rate-determining step being the conversion of the intimate ion pair to the solvent-separated ion pair.[17]

For the 2-adamantyl derivatives, the isotope effect found in 50 E (1.48) is close to the line, while the values for 70 E (1.59) and 80 E (1.68) fall off the line. However, none of the values for the 7-norbornyl derivatives fit. It seems apparent that these discrepancies could be due to primary isotope effect contributions caused by elimination in the rate-determining step.[13b] No elimination products were found in the solvolysis of compound **1** (R = Me). Ionization of compound **2** (R = Me) is immediately followed by rearrangement, thus preventing the occurrence of elimination in the rate-determining step.[27] In 50 E, 2-methyl-2-adamantyl chloride yields only 7% elimination product. However, in 70 E and 80 E increasing fractions of elimination were found to be associated with increasing β_{d_3} rate effects (see Table II).

The data for the 2-adamantyl derivatives listed in Table II can be readily accounted for in terms of the SBS correlation line, if allowance for rate-determining elimination is made. The α-CH_3/H ratio for this system has been estimated[8] to be 1.37×10^8, and the corresponding α-CH_3/CD_3 ratio is 1.46. This is very close to the observed α-CH_3/CD_3 in 50 E (1.48). The corresponding values in 70 E (1.591) and 80 E (1.681) are higher, but the olefin fractions are also larger, 0.25 and 0.33, respectively, indicating some contribution from rate-determining elimination. The fact that 2-methyl-2-chloroadamantane shows a higher olefin fraction than the corresponding bromide in 80 E indicates that the elimination in the tight ion pair probably involves attack by the leaving anion. The small amount of elimination in 50 E is probably derived completely from the solvent-separated ion pair since both chloride and bromide show the same olefin fraction. These results can be quantitatively analyzed using the following mechanistic scheme

$$RX \overset{K}{\rightleftharpoons} R^+X^- \overset{k_2}{\longrightarrow} R^+\|X^- \overset{k_{6S}}{\longrightarrow} \text{alcohol + ether}$$

$$\downarrow k_{5E} \qquad \downarrow k_{6E}$$

olefin olefin

and the equation published previously[20]

$$k_H/k_D = (K/K')r_{5E}(f'_{5E}/f_{5E})$$

where k_H/k_D is the observed isotope effect, K/K' is the isotope effect in the equilibrium formation of the tight ion pair, r_{5E} is the isotope effect for the elimination from the tight ion pair, and f'_{5E} and f_{5E} are the fractions of elimination in the deuterium and hydrogen compounds, respectively. If we assume that there is no isotope effect during the conversion of the tight to the solvent-separated ion pair ($r_2 = k_2/k_{2'} = 1$), and if f_2 and f'_2 are the fractions of reaction of the protio and deuterio compounds going *via* $k_{2'}$, then:

$$r_{5E}/r_2 = r_{5E} = \frac{f'_2 f_{5E}}{f_2 f'_{5E}}$$

By substitution, we obtain:

$$k_H/k_D = (K/K')(f'_2/f_2)$$

This equation can be used to calculate the expected solvolytic isotope rate effect from f_2 and f'_2 and the value of K/K' obtained from the SBS correlation. The fraction of reaction going via K_2 can be assumed to be the substitution product plus the small proportion of elimination obtained from the solvent-separated ion pair (k_{6E}) and observed in the reactions in 50 E (0.0753 and 0.026 for H and D compounds, respectively). The results are presented in Table V. It can be seen that within the accuracy of the experiments, the results agree with the K/K' value predicted from the SBS correlation and thus support the mechanistic analysis.

The observed CH_3/CD_3 values (1.84-2.10) for 7-methylnorbornyl tosylate are much larger in all solvents used than that predicted from the α-CH_3/H value of $10^{8.6}$ [28] and the correlation equation (1.49). However, as can be seen from Table VI, the observed isotope effects do not increase with

Table V. Calculated[a] and Observed Solvolytic Isotope Rate Effects for 2-Chloro-2-methyl-d_3-adamantane at 25°

Solvent	80 E	70 E	50 E
f_2[b]	0.72	0.806	1.00
f'_2	0.83	0.913	1.00
$(k_H/k_{d_3})_{obsd}$	1.68	1.59	1.48
$(k_H/k_{d_3})_{calcd}$	1.68	1.65	1.46

[a] Based on reaction scheme and equations given in the text. [b] Fraction of reaction going via the solvent-separated ion pair, the balance assumed to be going by elimination from the reversibly formed tight ion pair.

Table VI. Calculated[a] and Observed Solvolytic Isotope Rate Effects for 7-Methyl-d_3-7-norbornyl Tosylate

Solvent	HOAc	80 E	97 T	80 T
Temp, °C	70	40	20	20
f_S	0.29[b]	0.345	0.376	0.486
f'_S	0.49[b]	0.517	0.463	0.546
$(k_H/k_{d_3})_{obsd}$	1.94	1.84	2.10	2.00
$(k_H/k_{d_3})_{calcd}$	2.52	2.23	1.84	1.67

[a] Based on reaction scheme and equations given in the text. [b] Acetolysis products based on yields of alkene and acetate at 75°, ref 12.

increasing olefin fraction (decreasing f_S). Thus, although some elimination must occur in the rate-determining step (k_{5E}), a substantial amount of elimination arises also from the solvent-separated ion pair. Since this occurs in all solvents, it is not possible to estimate its contribution and make quantitative corrections for it as was done in the case of 2-adamantyl derivatives.

In the 2-methyl-2-adamantyl chloride, elimination at the tight ion-pair stage dominated that in the solvent-separated ion pair because of the relatively high basicity of the chloride leaving group which reacts here as a proton acceptor. However, with 7-methylnorbornyl tosylates, the lower basicity of the counter ion reduces the relative importance of the elimination from the tight ion pair, and relatively more of the observed elimination product arises from the solvent-separated ion pair formed after the rate-determining step. Thus, the calculated k_H/k_{d_3} values in Table VI show only approximate agreement with the actually measured isotope effect and tend to decrease with decreasing olefin fraction.

From all the presently available data, it is reasonable to assume that the SBS correlation holds for all reactions where the formation of the tight ion pair (k_1) or the formation of the solvent-separated ion pair from the tight ion pair (k_2) is the rate-determining step for both the hydrogen and the α-methyl compounds.[29]

While it is apparent that in SN2 reactions both the α-CH_3/H effects and α-CH_3/CD_3 effects are small, the indications are that these reactions do not follow the SBS correlation. This is not surprising in as much as it is generally accepted that there is a relatively large steric effect on the SN2 reaction rates caused by α-methyl substitution.[30] This also holds for neighboring group participation reactions of the "internal SN2 type".[31] The rates and isotope effects for remote methyl groups conjugated to the reaction center do not fall on the SBS correlation line.[32]

The large α-CH_3/H rate ratio and the large isotope effect for the 7-norbornyl derivatives and the 2-adamantyl derivatives indicate that the corresponding carbonium ions show unusually large electron demand. Similarly, large CD_3 isotope effects were observed in the formation of some vinyl cations.[36]

The high electron demand of the 7-norbornyl cations is also reflected in the low solvolytic reactivity of the corresponding esters.[25] This has been explained as being due to the small ring angle at the 7 position and the consequent increase in angle strain in going to the trigonal carbonium ion.[37] More recently, orbital-symmetry arguments have been used to explain this phenomenon.[38]

The 2-adamantyl system shows a more interesting pattern in that the solvolysis rates of the tertiary derivatives are approximately ten times faster than those of the corresponding *tert*-butyl analogs.[8] Thus, Schleyer's suggestion that the low α-CH_3/H ratio for the isopropyl-*tert*-butyl pair is largely due to nucleophilic acceleration by solvent of the isopropyl reaction rate is not reflected in the α-CH_3/CD_3 isotope effects, which are lower for the *tert*-butyl case (1.33) than for 2-adamantyl (1.46). These values and the SBS correlation indicate that the "true" α-CH_3/H ratios for the carbonium ion type solvolyses are 10^6 for *tert*-butyl and $10^{8.1}$ for 2-methyl-2-adamantyl. The large electron demand in the 2-adamantyl case must be either due to a mechanistic difference, which seems unlikely, or to steric inhibition of solvation. If steric inhibition of solvation increases the electron demand, its effect on the rate must somehow be compensated, perhaps, by steric acceleration in both the secondary and tertiary adamantyl derivatives.

Experimental Section

3,3-Dimethyl-2-butanol. 3,3-Dimethyl-2-butanone (pinacolone) was reduced with $LiAlH_4$ in diethyl ether in the usual manner. The alcohol was distilled through a spinning band column. The center cut (bp 119°) represented 37% yield. The ir spectrum showed no absorption due to the carbonyl group. NMR ($CDCl_3$) showed δ 0.90 (s, 9), 1.08 (d, 3), 3.4 (q, 1), 4.01 (s, 1).

3,3-Dimethylbutan-*1,1,1-d*$_3$-2-one. Pinacolone (0.2 mol) was stirred for 24 hr in a mixture of D_2O (25 ml) and a stock solution of deuterated acid (25 ml). The acid solution was prepared by adding 4 g of PCl_5 to 200 ml of D_2O. After five exchanges, the deuterium content in the β position was shown by NMR to be greater than 98.5%: NMR δ 1.02 (s).

3,3-Dimethylbutan-*1,1,1-d*$_3$-2-ol. This compound was prepared from 3,3-dimethylbutan-*1,1,1-d*$_3$-2-one in the same manner that 3,3-dimethyl-2-butanol was prepared, in 72% yield: NMR ($CDCl_3$) δ 0.91 (s, 9), 3.40 (s, 1), 4.00 (s, 1).

3,3-Dimethyl-2-butyl *p*-Brombenzenesulfonates. The hydrogen and β-d_3 compounds were prepared from the alcohols by the usual Tipson procedure[39] and recrystallized from petroleum ether (30–60°). Hydrogen compound: yield 53%; mp 52.5–53.2° (lit.[40] mp 53.2–53.5°); NMR ($CDCl_3$) δ 1.25 (d, 3), 4.44 (q, 1), 6.80 (m, ~5). β-d_3 compound: mp 51.5–52.5°; NMR ($CDCl_3$) δ 0.87 (s, 9), 4.45 (s, 1), 7.72 (q, 4).

2,2-Dimethyl-1-propyl *p*-Brombenzenesulfonate. This compound was prepared by a modification of the Tipson procedure.[39] To 3.8 g (0.015 mol) of *p*-bromobenzenesulfonyl chloride in 10 ml of dry CH_2Cl_2 was added 1.2 g (0.015 mol) of dry pyridine. The solution was cooled to 0°, and 1.3 g (0.015 mol) of 2,2-dimethylpropanol was added. The mixture was kept at 0° for 3 days during which time the solution turned dark, and the pyridine–HCl crystals separated. These crystals were filtered off, and the CH_2Cl_2 solution was extracted with 2 *N* H_2SO_4. The solution was filtered and CH_2Cl_2 removed under reduced pressure. The solid residue was recrystallized from hot petroleum ether to give 3.7 g (81%) of product: mp 70–71°; NMR ($CDCl_2$) 8.92 (s, 9), 3.72 (s, 2), 7.75 (~s, 4).

2-Methyl-2-adamantanol. The following procedure[41] was used. To the Grignard reagent prepared from 1.21 g (0.05 g-atom) of Mg and 7.1 g (0.05 mol) of methyl iodide in 55 ml of anhydrous diethyl ether was added a solution of 1.5 g (0.01 mol) of 2-adamantanone in 10 ml of anhydrous diethyl ether. The reaction mixture was refluxed for 2 hr. The complex was hydrolyzed with a saturated aqueous solution of NH_4Cl and with ice. The ether solution was washed in succession with water, a 2% solution of Na_2CO_3, and with water and dried over a mixture of $MgSO_4$ and K_2CO_3. Ether was removed at reduced pressure, and the alcohol was recrystallized from a 1:1 mixture of pentane and hexane (Dry Ice–acetone) to yield 0.995 g (60%), mp 205–206° (sealed capillary). The ir spectrum showed no absorption due to the carbonyl group. NMR: (CCl_4) δ 1.22 (s, 1), 1.27 (s, 3), 1.20–2.46 (m, 14).

2-Methyl-*d*$_3$-2-adamantanol.[42] This compound was prepared in

the same manner as the hydrogen analog. The ir spectrum showed no absorption due to the carbonyl group. NMR (CCl_4): δ 1.21 (s, 1), 1.20–2.48 (m, 14).

2-Methyl-2-adamantyl Chlorides. The hydrogen and the methyl-d_3 compounds were prepared in the same way.[41] Gaseous HCl was bubbled for 2 hr through a solution of the alcohol (4.82 mmol) in 20 ml of pentane. The solution was dried over a mixture of K_2CO_3 and $CaCl_2$, pentane was removed under reduced pressure, and the chloride was recrystallized from pentane (Dry Ice–acetone), yield 98%, mp 176–176.5° (sealed capillary). The ir spectrum showed no absorption due to the OH group. Hydrogen compound: NMR (CCl_4) δ 1.40–2.75 (m, ~14), 1.76 (s, ~3). Methyl-d_3 compound: NMR (CCl_4) δ 1.38–2.73 (m).

2-Methyl-2-adamantyl Bromide. The bromide was prepared by bubbling gaseous HBr through a solution of the alcohol (0.5 g, ~3 mmol) in 25 ml of ether at 25° fo 30 min. The aqueous layer was removed and the other layer treated with potassium carbonate. The ether was removed under reduced pressure, and the crude product was sublimed: purified yield, ~40%; mp 133–137° (sealed capillary): NMR ($CDCl_3$–TMS) δ 1.45–2.8 (m, −14), 2.11 (s, 3); ir showed no O–H or C–O stretch.

7-Methyl-*anti*-7-norbornenol and 7-Methyl-d_3-*anti*-7-norbornenol. These compounds were prepared from 7-norbornenone[43] according to a previously published procedure.[44]

7-Methyl-*anti*-7-norbornenyl *p*-Nitrobenzoates. The hydrogen and the methyl-d_3[42] compounds were prepared from the alcohols using the same procedure.[45] *p*-Nitrobenzoyl chloride (2.70 g, 0.014 mol) and 7-methyl-*anti*-7-norbornenol (2.00 g, 0.016 mol) were dissolved in pyridine (20 ml), and the solution was stirred at room temperature for 24 hr. It was then poured into ice and water and extracted with diethyl ether. The ether solution was washed in succession with 2 *N* HCl, a saturated aqueous solution of $NaHCO_3$, and water and dried over $CaSO_4$. The ether was removed under reduced pressure, and the *p*-nitrobenzoate was recrystallized from acetone–water to yield 3.15 g (79.4%), mp 126.5–127.5°. The ir spectrum showed no absorption due to the OH group. Hydrogen compound: NMR (CCl_4) δ 1.05 (m, 2), 1.56 (s, 3), 1.85 (m, 2), 3.10 (m, 2), 6.10 (m, 2), 8.21 (m, 4). Methyl-d_3 compound: NMR (CCl_4) δ 1.03 (m, 2), 1.84 (m, 2), 3.08 (m, 2), 6.08 (m, 2), 8.20 (m, 4).

7-Methyl-7-norbornyl Tosylates. The hydrogen and the methyl-d_3[42] compounds were prepared from the alcohols in the same manner. The alcohols were prepared according to published procedures.[44] 7-Methyl-7-norbornanol (3.48 g, 0.0276 mol) was dissolved in 16 ml of pyridine, and the solution was cooled to −5°. *p*-Toluenesulfonyl chloride (6.40 g, 0.0336 mol) was added to the solution and stirred until it dissolved. The reaction mixture was kept at 0° for 48 hr, then cold water and crushed ice were added until there was no more precipitation of the tosylate. The precipitate was removed by filtration, washed with water, and dissolved in pentane, and the solution was dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was cooled with Dry Ice–acetone. Pentane was removed from the crystalline tosylate precipitate, and the recrystallization was repeated three more times to yield 5.02 g (65%), mp 46–47° (lit.[7a] mp 48–49°). The ir spectrum showed no absorption due to the OH group. Hydrogen compound: NMR (CCl_4) δ 1.00–2.38 (m, 10), 1.62 (s, 3), 2.94 (s, 3), 7.50 (m, 4).

Kinetic Procedure. Two different previously published procedures were used for the kinetic measurements: the conductance method[21,22] for the neopentyl and 2-adamantyl derivatives and continuous potentiometric titration[23] for the 7-norbornyl derivatives. The rates for the 7-methyl-*anti*-norbornenyl compounds were determined by potentiometric titration of the acid developed in ampoules taken out of the constant temperature bath in given time intervals. The rate constants were calculated from the standard integrated first-order law using a nonlinear least-squares program. No trend was observed in the rate constant between 20 and 80% of reaction completion.

Product Determinations. Solutions of 0.1 mmol of 2-methyl-2-adamantyl chloride and bromide in 1 ml of each solvent were solvolyzed in a 25° constant-temperature bath through more than 10 half-lives. Each solution contained an equimolar amount of 2,6-lutidine. The product ratios were determined by VPC on a 4 ft × 1/16 in. UCON column at a column temperature of 128°. The peak integrations (FID) were used directly for the determinations. The order of elution was olefin, ether, alcohol.

7-Methyl-7-norbornyl tosylate was solvolyzed for 10 half-lives in the presence of 2,6-lutidine. The reaction mixture was diluted with water and extracted with diethyl ether, and the combined ether extracts were washed with water and dried. After careful removal of the solvent through a Vigreux column, the residue was analyzed by VPC on a 5-ft SE-30 column at 70°. The products (olefin and alcohol) were compared with authentic samples (VPC retention time and NMR), and the trifluoroethyl ether was analyzed by MS coupled with the VPC instrument. The peak integrations were used directly for determinations of the amount of each product.

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References and Notes

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(29) In a recent article, Gassman[12] has indicated an α-CH_3/H *vs.* α-CH_3/CD_3 plot which differs substantially from the SBS correlation. One of the three points which form the basis of his line was that for 7-methylnorbornyl tosylate which we have shown to deviate because of rate-determining elimination. The center point for *anti*-7-methyl-*syn*-7-tosyloxynorbornene deviates from the line by approximately one power of ten assuming that the value for k_{CH_3/CD_3} is accurate enough. This vertical dis-

placement can be rationalized as being due to steric acceleration of ionization[9a] (exo hydrogens syn to the methyl group). The third point was for the *anti*-7-norbornenyl system for which our results given above indicate good agreement with the SBS correlation. However, we disagree both with respect to the Me/H ratio which was obtained by a rather elaborate extrapolation (see ref 17 on p 7803 of ref 12) and with the reported α-CH_3/CD_3 isotope effect. This effect was observed in the *p*-nitrobenzoates solvolyzed at 135° in 70% aqueous dioxane where complications due to acylcarbon oxygen cleavage may arise.

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Free-Radical Coupling, Cleavage, and Redox Reactions in ^{60}Co γ Radiolysis of Aqueous Methyl Acetate. Effects of Additives

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Abstract: Reaction of methyl acetate with e^-_{aq} may lead to $CH_3C(O^-)OCH_3$ (I^-), $CH_3C(OH)OCH_3$ (II), and CH_3CO (IIA), and with ·OH and H· to $\cdot CH_2CO_2CH_3$ (III), and to $CH_3CO_2CH_2\cdot$ (IV). Methyl acetate is consumed, $G = -3.5$, and the loss is decreased by formate which scavenges ·H and ·OH, and increased by N_2O which converts e^-_{aq} to ·OH. Hydrogen is formed, $G = 1.1$, and this is decreased by scavengers for H·, and increased by H^+ which converts e^-_{aq} to H·. In radiolysis of 0.027 *M* methyl acetate, 1.5×10^{22} eV/l., radical combination products are: ethylene diacetate ($CH_3CO_2CH_2CH_2O$-$COCH_3$) (EDA), $G = 0.48$, from IV + IV; methyl β-acetoxypropionate ($CH_3CO_2CH_2CH_2CO_2CH_3$) (MAP), $G = 0.28$, from IV + III; dimethyl succinate (DMS), $G = 0.05$, from III + III; and a mixture of methyl acetoacetate and acetonyl acetate (MAA and AA), $G = 0.07$. Biacetyl is not observed. β-Mercaptopropionic acid, 0.0005 *M*, prevents formation of coupling products, as it reduces radicals III and IV, and thiyl radical oxidizes radical II back to methyl acetate. In a damaging cleavage, mercaptan reduces II and IIA to acetaldehyde, which is not formed in the absence of mercaptan. Biacetyl, H^+, N_2O, and H_2O_2 remove e^-_{aq} and I^-, II and IIA, and suppress MAA–AA; H^+ increases H·, III, and MAP, and DMS; N_2O and H_2O_2 increase ·OH, IV, and EDA. 2-Propanol, HCO_2^-, and CO scavenge ·OH and H· and suppress coupling products. Other sources of ·OH, Fenton's reagent and H_2O_2–uv, lead to EDA, MAP, and DMS with a high IV/III ratio. H· preferentially attacks acyl C–H; ·OH preferentially attacks alkoxyl C–H. Cleavage products (acetic acid, $G \sim 1.5$; methanol, $G \sim 1.0$) and small yields of methane and formaldehyde are found. Scavengers of e^-_{aq} or of H· and ·OH decrease acetic acid by half. Scavenging of all three fragments prevents formation of acetic acid, and hydrogen peroxide increases it. Radicals II and IIA may lead to ¾ of the acetic acid, IV to the remainder. Oxidation of them, largely by radical III, and in part by H_2O_2, is the suggested mechanism. Much of radical III is reduced back to methyl acetate. Cu^{2+}–Cu^{1+} strongly decrease coupling products and increase acetic acid, probably oxidizing IV and reducing III. Yields of radicals involved in formation of coupling products and acetic acid are estimated: G(II and IIA) = 1.2; G(III) = 1.4; G(IV) = 1.7. Part of the radicals, $G \sim 1.6$, regenerate methyl acetate by self-repair reduction of IV and III by II. Deuterium is introduced into methyl acetate during radiolysis in D_2O.

The effects of high-energy radiation on simple organic compounds in dilute aqueous solution are of interest, intrinsically and with respect to implications about corresponding reactions of high molecular weight materials and compounds of biological importance. In ^{60}Co γ irradiation of ~0.01 *M* aqueous solutions, >99.9% of the energy is absorbed by the water, leading to the reactive fragments,[1] the solvated electron, hydroxyl radical, and hydrogen atom, in molecules per 100 eV[2] [$G(e^-_{aq}) = 2.65$, G(OH) = 2.72, G(H) = 0.55], and to molecular products, hydrogen and hydrogen peroxide [$G(H_2) = 0.45$, $G(H_2O_2) = 0.68$]. The γ-ray-induced transformations of the solute result from their free radical-type reactions with the radiolytic products of the water.

Additives which scavenge or interconvert the reactive fragments modify the reactions and may indicate the nature of the reaction of the solute with each of the fragments. Formate ion removes H·, $k = 2.5 \times 10^9\ M^{-1}\ sec^{-1}$, and ·OH, $k = 2.2 \times 10^8\ M^{-1}\ sec^{-1}$, leading to $\cdot CO_2^-$.[3] Nitrous oxide reacts with e^-_{aq}, leading to ·OH and N_2,[3,4] $k = 8.7 \times 10^9\ M^{-1}\ sec^{-1}$. Hydrogen peroxide reacts with e^-_{aq} and H·, leading to ·OH[3,5] with rate constants $1.2 \times 10^{10}\ M^{-1}\ sec^{-1}$ and $5 \times 10^7\ M^{-1}\ sec^{-1}$, respectively, and with ·OH, leading to $HO_2\cdot$,[3,6] $k = 4.5 \times 10^7\ M^{-1}\ sec^{-1}$. Mercaptan (RSH) reacts with the three fragments:[3,7] e^-_{aq} leads to HS^- and R·, $k = 5.0 \times 10^9\ M^{-1}\ sec^{-1}$; ·OH leads to RS·, $k = 3.0 \times 10^9\ M^{-1}\ sec^{-1}$; H· leads to R· and RS·, $k = 2.5 \times 10^9\ M^{-1}\ sec^{-1}$. Mercaptans and thiyl radicals also have high reactiv-