Methyl Radical Attack on Methanol, Ethanol, and Isopropyl Alcohol

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THE reactions of methyl radicals with three alcohols in the gas phase have been studied[1] to determine the main points of attack in the molecules. Two radical sources, acetone and [$^2H_6$]acetone, were used since an isotopic-exchange reaction between the alcoholic hydroxy-group and acetone invalidates results if the hydroxy-group and the radical source are isotopically labelled (H or D) in opposite senses, a situation not previously recognized.[2,3] This restriction on the choice of substrate and radical source hinders the accurate measurement of data on the attack on the hydroxy-groups.

The most important reaction in the alcohols is the attack on the α-hydrogen atom, in the temperature range involved (130—250°). The equations below indicate the systems studied (the overall reaction with unlabelled alcohols was studied[1] but these results will not be presented here):

$$CD_3 + CH_3OD \rightarrow CD_3H + \dot{C}H_2OD \qquad (1)$$

$$Me\cdot + CD_3OH \rightarrow MeD + \dot{C}H_2OH \qquad (2)$$

$$CD_3 + C_2H_5OD \rightarrow CD_3H + CH_3\dot{C}HOD \qquad (3)$$

$$Me\cdot + MeCD_2OH \rightarrow MeD + Me\dot{C}DOH \qquad (4)$$

$$CD_3 + i\text{-}C_3H_7OD \rightarrow CD_3H + i\text{-}C_3H_6OD \qquad (5)$$

$$Me\cdot + Me_2CDOH \rightarrow MeD + \dot{C}Me_2OH \qquad (6)$$

The Arrhenius activation energies, *A*-factors, and rate constants at 182° are listed in the Table. Of the three alcohols only methanol has been studied in detail before.[2,4] One of the investigations[4] is in good agreement with this work; the other[2] probably suffers from the isotopic exchange mentioned above. In ethanol, the $CH_3^{\cdot}$ group was found to be ten times less reactive than the CH_2 group and the Arrhenius parameters shown for reaction (3) apply (within experimental error) to the alkyl group as well. In isopropyl alcohol [reaction (5)], no correction can be made to the alkyl group reactivity for the methyl groups since secondary reactions interfere, however the reactivities of the alkyl and CH groups should be even closer than in ethanol.

TABLE

Reaction	$\log_{10} A$ (cm.$^{-3}$ mole^{-1} sec.$^{-1}$)	E(kcal. mole^{-1})	$\log_{10} k$ (182°)	
			overall	per atom
(1)	11·3 ± 0·1	10·0 ± 0·1	6·43	5·96
(3)	11·6 ± 0·1	9·7 ± 0·3	6·94	6·64
(5)	11·2 ± 0·1	7·9 ± 0·2	7·36	7·36
(2)	11·3 ± 0·1	11·9 ± 0·2	5·60	5·13
(4)	11·6 ± 0·1	11·4 ± 0·1	6·14	5·84
(6)	11·3 ± 0·1	9·7 ± 0·1	6·62	6·62

The results show quite clearly that the α-hydrogen or deuterium atoms become more reactive with increasing methyl substitution. The relative reactivities of the α-H atoms, at 182° on a per-atom-available basis, are 1 : 5 : 25 in reactions (1), (2), and (3) respectively; the figures are similar in the deuteriated alcohols. The relative reactivities[5] of the α-hydrogen atoms in the hydrocarbon series ethane, propane and isobutane are 1 : 7 : 50. The differences between the ratios for ROH and RMe reflect the greater activating effect of the hydroxy-group over the methyl group in the *first* members (methanol and ethane) of the two series.

The isotope effects in all three alcohols are larger than expected. Although the ratios A_H/A_D are unity, $E_D - E_H$ is larger than the zero-point-energy difference for CH and CD bonds of 1·2 kcal. mole^{-1}, being 1·9 ± 0·3, 1·7 ± 0·3, and 1·8 ± 0·2 kcal. mole^{-1} for methanol, ethanol and isopropyl alcohol respectively. This may be a consequence of quantum-mechanical tunnelling.

A secondary radical attack on isopropyl alcohol [reaction (7)] occurred following the primary attack [reaction (5)], increasing the apparent abstraction from the hydroxy-group. A spurious secondary isotope effect resulted at the hydroxy-group between the species Me_2CDOH and

$$Me + Me_2COH \longrightarrow MeH + MeCOMe \qquad (7)$$

Me_2CHOH assuming that the isopropyl group has the same reactivity in the unlabelled alcohol as in Me_2CHOD. Since no such effects were observed in methanol or ethanol, it seems safe to assume that the equivalent secondary reactions are unimportant there, as expected.[6] It is also clear that the secondary reaction has no effect on the alkyl group reactions since the rate-constants are internally self-consistent among the three different isotopic species in each case, while the activation energies for hydrogen abstraction from the alkyl groups of the alcohols and their corresponding dialkyl ethers are identical.[1,7] The possibility arises that secondary reactions are important in the reaction of CF_3 radicals with methanol[8] where low activation energies and A-factors have been reported for attack on the hydroxy-group. Similar low Arrhenius parameters were found in this work[1] for the attack on the hydroxy-group of isopropyl alcohol but not of methanol or ethanol.

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