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THE DEUTERIUM ISOTOPE EFFECT IN THE PERMANGANATE OXIDATION OF AROMATIC TRIFLUOROMETHYL ALCOHOLS

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PHENYL trifluoromethyl carbinols are oxidized by aqueous alkaline permanganate to the corresponding ketones. We wish to report a kinetic isotope effect of unusual size for the reaction of the 1-deuterio analogs of these compounds.

$$YC_6H_4CDOHCF_3 + 2MnO_4^- + 2OH^- \longrightarrow YC_6H_4COCF_3 + 2MnO_4^= + H_2O + HDO$$

1-Phenyl-2,2,2-trifluoroethan-1-ol (I) and its p-methyl (II) and m-bromo (III) derivatives were prepared by $LiAlH_4$ reduction of the corresponding ketones. (II), b.p., 94.5 (12 mm) $n_D^{24} = 1.4650$. Found: C, 57.1; H, 5.0. $C_9H_9F_3O$ requires C, 56.9; H, 4.7. Phenylurethan of (II), m.p., 104-105. Found: C, 62.1; H, 4.5; N, 5.1. $C_{16}H_{14}F_3O_2N$ requires C, 62.1; H, 4.5; N, 5.1. (III), b.p. 115 (12 mm), $n_D^{27} = 1.5005$. Found: C, 38.0; H, 2.5; Br, 31.6. $C_8H_6F_3BrO$ requires C, 37.1; H, 2.4; Br, 31.4.

p-Tolyl trifluoromethyl ketone[1] was prepared from p-tolyl magnesium bromide and trifluoroacetic acid. Bromination of phenyl trifluoromethyl

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[1] J.D. Park, H.A. Brown and J.R. Tacker, J.Amer.Chem.Soc. **73**, 709 (1951)

ketone gave the m-bromo derivative, b.p., 83.5 (12 mm), $n_D^{24} = 1.5030$. Found: C, 38.2; H, 1.6; F, 20.6. $C_8H_9OF_3Br$ requires C, 38.0; H, 1.5; F, 22.5. 2,4-Dinitrophenylhydrazone, m.p. 121.5-123. Found: C, 38.8; H, 2.5; N, 12.0; F, 12.0. $C_{14}H_8O_4N_4F_3Br$ requires C, 38.6; H, 1.9; N, 12.9; F, 13.2.

1-Phenyl-2,2,2-trifluoroethan-1-ol-1-d and its p-methyl and m-bromo derivatives were prepared by $LiAlD_4$ reduction. The infrared spectra of these compounds were identical with those of their protio analogs, I, II and III, except for the shift of the C-H stretching band from 2895 cm^{-1} to 2150 cm^{-1}.

The purity of the alcohols was checked by vapour phase chromatography and samples for reaction were collected in several cases by this means. The reaction was followed as previously described[2]. The oxidation in aqueous solution follows the rate law

$$V = k\,[ArCHOHCF_3][MnO_4^-][OH^-]$$

for both the protio and deuterio compounds with the following rates.

Permanganate oxidation rates in 0.2 M NaOH at 25

	k_H l.mole^{-1}sec^{-1}		k_D l.mole^{-1}sec^{-1}	$\frac{k_H}{k_D}$
$C_6H_5CHOHCF_3$	7.5	$C_6H_5CDOHCF_3$	0.47	16.0
$p\text{-}CH_3C_6H_4CHOHCF_3$	8.4	$p\text{-}CH_3C_6H_4CDOHCF_3$	0.52	16.1
$m\text{-}BrC_6H_4CHOHCF_3$	7.6	$m\text{-}BrC_6H_4CDOHCF_3$	0.47	16.2

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[2] R. Stewart, J.Amer.Chem.Soc. **79**, 3057 (1957)

The magnitude of the isotope effect[3] can be explained on either of the following grounds. Either the reaction is a complex one involving consecutive dependent steps such that the overall isotope effect is a cumulative one or the reaction is occurring with loss of the bending modes of the carbon-hydrogen bond in the transition state in addition to the loss of the stretching mode.

The acidity of these alcohols (pK_a = 11.9, 12.0 and 11.5 for I, II and III) is such that they exist largely as their anions under the oxidation conditions. A transfer of hydride ion from the alkoxide ion to Mn(VII), favoured for the analogous benzhydrol system,[2] is difficult to reconcile with the relative indifference of the reaction rate to nuclear substitution. A more complete discussion of the mechanism will be published later.

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[3] K.B. Wiberg, Chem.Rev. **55**, 713 (1955).