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KINETICS OF DEDEUTERATION OF BENZENOID HYDROCARBONS

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IN connection with our studies of reactivity of benzenoid hydrocarbons and their derivatives, we have dealt with the kinetics of dedeuteration of monodeuterated hydrocarbons. Lately, several hydrocarbons have been investigated (1-7); for a similar study on deuteration see Ref. (8). Very recently two papers by Streitwieser et al. (9,10) appeared in which the deuterium exchange in methylarene-α-d's was studied. These works prompt us to publish our results.

The following first-order rate constants (sec^{-1}) of dedeuteration in the mixture of 91.8 mol. % CF_3COOH, 2.5 mol. % $HClO_4$, and 5.7 mol. % H_2O at 30 ± 0.1°C were obtained (substrate, log k, class[++] of position in which deuterium is attached): benzene-d, -5.81 ± 0.01, 0; naphthalene-2-d, -4.06 ± 0.02, 0; biphenyl-4-d, -4.00 ± 0.01, 0; naphthalene-1-d, -3.12 ± 0.01, 1; biphenyl-2-d, -4.03 ± 0.02, 1; phenanthrene-9-d, -3.10 ± 0.02, 1; anthracene-1-d, -2.53, 1; anthracene-9-d, -1.58 ± 0.04, 2.

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[++] 0 benzene type, 1 α-naphthalene type, 2 meso-anthracene type position.

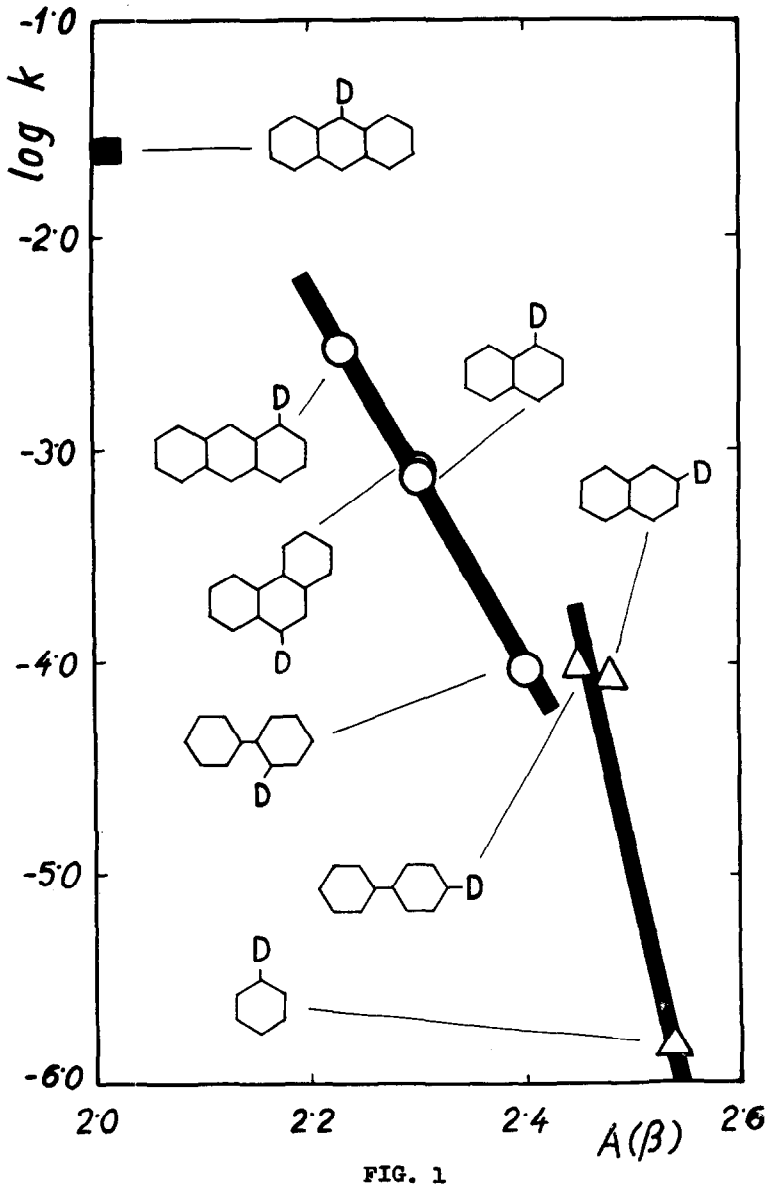

FIG. 1

Logarithms of dedeuteration rate constants plotted against Wheland atom localisation energies A (11,12). Designation (class) (11): △ (0), ○ (1), ■ (2).

The deuterated hydrocarbons were synthesized from the corresponding Grignard or lithium compounds by action of D_2O or CH_3COOD. The reaction course was followed mass-spectrometrically.

From the plot of log k vs. Wheland atom localisation energies A (11,12) it is evident that these quantities are correlated (Fig. 1). However, it seems probable that the data can be divided into three groups according to the class (11) of the position where deuterium is bound. This is in agreement with similar plots for other electrophilic substitution reactions (e. g., deuteration (8), nitration (13), see also (14)).

A discussion of these and further results, details on experimental technique and a study of infrared spectra of deuterated hydrocarbons will be published later.

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