Protiodetritiation of Benzene in Trifluoroacetic Acid

By HERBERT V. ANSELL and ROGER TAYLOR*

(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ, *Sussex*)

Summary Rates of protiodetritiation of benzene in trifluoroacetic acid, measured over a wide temperature range, confirm that the rate coefficient at 70° is $9{\cdot}5 \times 10^{-9}\,s^{-1}$; consequently there is no need to amend the literature partial rate factors appropriate to this condition, as implied in recent publications.

PROTIODETRITIATION of aromatic hydrocarbons in anhydrous trifluoroacetic acid at 70° has become the most commonly used condition for studying hydrogen exchange and almost 200 partial rate factors relating to this condition are now available.[1–3] This is the widest range of data available under one condition for any electrophilic substitution, and in view of the pre-eminence of hydrogen exchange as a model reaction for evaluating theories of electrophilic aromatic substitution (*e.g.* ref. 4), the need for accuracy in these factors is paramount.

TABLE

Rate coefficients for protiodetritiation of $[^3H_1]$benzene in CF_3CO_2H

T/°C	..	70	90	110	125	140	150	180
$10^7k/s^{-1}$	..	0·095	0·585	2·57	7·47	19·25	33·7	125

Difficulty in measuring the rate coefficient for benzene arises from the slowness of reaction ($t_{\frac{1}{2}}$ *ca.* 2 years), and the literature value[5] of $9{\cdot}5 \times 10^{-9}$ was obtained from measurements on 4 pairs of sealed ampoules which, opened at $t = 0$ and $t = 16$ weeks, gave individual rate coefficients of 9·6, 9·3, 9·45, and 9·5 (all $\times 10^{-9}$, in s^{-1}). Recently, Wright *et al.*[6] have suggested that this value is considerably in error, and they propose a new value of $4{\cdot}9 \times 10^{-9}$, based upon two individual rate coefficients of $7{\cdot}19 \times 10^{-9}$ and $3{\cdot}69 \times 10^{-9}$, the former run being followed over an 8-month period. (By contrast, Streitwieser *et al.*[3] suggested that the original value might be too *low* since a plot of partial rate factors in hydrogen exchange *vs.* those from acetolysis of arylmethyl tosylates was curved. This could however easily arise from different demands for resonance in these two reactions, and indeed a plot of the hydrogen exchange data against σ^+ values is linear.)[2]

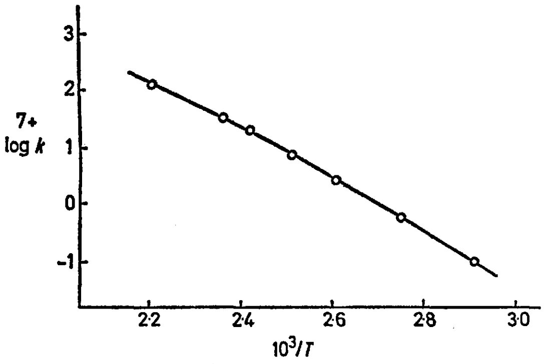

FIGURE. Arrhenius diagram for detritiation of benzene in anhydrous trifluoroacetic acid.

Some indication (apart from the very poor reproducibility) that the newly proposed value is wrong is indicated by the following: (i) Plots of partial rate factors obtained between pairs of methylated aromatics (log $k[ArMe_n]/k[ArMe_{n-1}]$, $n = 0$—6) *vs.* the reactivity of the less reactive compounds are reasonable straight lines except that the factors derived between toluene and benzene are well off the line[6] showing the new benzene rate coefficient to be too low. (ii) Rates of detritiation of benzene, *p*-xylene, hemimellitene (4-position), durene, mesitylene, isodurene, and pentamethylbenzene correlate linearly with the deuteration data for the same aromatics in aqueous trifluoroacetic acid,[7] provided that the original rate coefficient for benzene is used; with the alternative lower rate coefficient the correlation is poorer.

We have now measured the rates of protiodetritiation of benzene in trifluoroacetic acid at temperatures between 70 and 180° (Table and Figure). The run at 70° was carried out over a 10-month period using the sealed tube technique[8] modified in that ampoules removed from the thermostat were kept refrigerated until the end of the run. All samples were then worked up together. This avoided the possibility of evaporation of benzene from the toluene extracts which would lead to erroneously low rate coefficients. Excellent first-order plots were obtained at all temperatures, and the rate coefficient at 70° is exactly† that obtained previously by Baker and Eaborn,[5] so that the partial rate factors in the literature require no modification. The accuracy of the 70° value is shown by the absence of any deviation of it from the Arrhenius plot. This latter is very slightly curved over the range of higher temperatures (as are the Arrhenius plots for some other compounds, the kinetics for which will be described in a subsequent publication) and this most probably arises from decrease in the acidity function with increasing temperature.[9]

Our work does show however that the literature values[10] for detritiation of benzene at 110·15 and 128·25° are in error (being too high) as is therefore the activation energy (23·8 kcal/mol) calculated[1a] using these values and the 70° rate coefficient; over the 70—125° range the activation energy is 21·6 kcal/mol.

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† Since more recent work on detritiation in trifluoroacetic acid has tended to produce rates 5—10% lower than the original values (owing most probably to greater purity of the acid), this exact agreement may be fortuitous.

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