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Hydrogen Isotope Exchange between Fluoroform (CF_3H) and Water. 1. Catalysis by Hydroxide Ion[1]

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Abstract: The solubility of gaseous CF_3H in water and sodium hydroxide solutions has been measured as a function of temperature (20–85 °C) and NaOH concentration (0–1.9 $\text{mol}\cdot\text{L}^{-1}$). These data enabled conversion of the observed rate constants for H/D isotope exchange between CF_3H and D_2O, obtained in a stirred gas/liquid reactor, to in-solution values. Although catalysis of exchange by hydroxide ion is extremely slow at ambient temperature, because of the high activation energy (134 $\text{kJ}\cdot\text{mol}^{-1}$), the reaction rate becomes measurable above 50 °C. At 80 °C the in-solution rate constant k_2 is $2.1 \times 10^{-3}\ \text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$. The reaction is first order in hydroxide ion and ΔS^* is 75 $\text{J}\cdot\text{mol}\cdot\text{K}^{-1}$. CF_3H hydrolysis in these alkaline solutions has been shown to be a factor of about 10^4 slower than isotope exchange. On the basis of a revised value of 27 (Streitwieser scale) for the pK_a of CF_3H, pK_a's were estimated for a series of nine trihalomethanes from kinetic exchange data available in the literature.

Marling, Tuccio, and co-workers have suggested[2,3] that fluoroform gas (CF_3H, D) could be suitable for use in a deuterium separation process based on isotopically selective IR multiple-photon-induced dissociation of this molecule. The economic viability of such a process would depend on various factors. One requirement is a fast redeuteration of the residual CF_3H, preferably via contact with water. Several other haloforms, like chloroform (CCl_3H), undergo fairly rapid hydrogen isotope exchange in *alkaline* aqueous solutions;[4,5] however, the limited data in the literature for CF_3H suggest that its exchange reactivity is negligible in hydroxide ion/water solution at ambient temperature.[5] A solution of K_2PtCl_4 with DCl in 1:1 (mole) CH_3COOD/D_2O at 100 °C was found to be a very poor catalyst for CF_3H exchange with water—reactivity was greater for CH_4.[6]

Andreades studied base-catalyzed deuterium exchange between methoxide/methanol solutions and a series of monohydrofluorocarbons, including fluoroform.[7] CF_3H was the least reactive in the series (rate constant measured at 70 °C), but it is not clear that those results reported for the *gaseous* substrates including CF_3H are in-solution rate constants. In any case, because the CF_3H and other gaseous substrates were not continuously mixed with the catalyst solutions during the runs, it is possible that the resultant rate constants are partially diffusion-limited rather than reaction rate-limited values (see below).

We have determined that CF_3H *does* undergo hydrogen isotope exchange with $NaOD/D_2O$ solution above ambient temperature. This reaction has been studied in detail as a function of temperature and catalyst concentration by using a stirred gas/liquid reactor. CF_3H solubility has been measured for water and a series of hydroxide ion/water solutions, to enable calculation of true in-solution rate constants. The results of this study, including an analysis of the significance of CF_3H hydrolysis relative to isotope exchange, are reported here.

The addition of dimethyl sulfoxide (Me_2SO) to alkaline aqueous solution is known to enhance base-catalyzed hydrogen-exchange reactivity for many substrates such as chloroform[8] and molecular hydrogen.[9] The effect of added Me_2SO on the CF_3D exchange rate constant, the activation parameters, and the kinetic isotope effect are reported in part 2 of this series.[10]

Experimental Section

Reagents. Fluoroform was used as received from Matheson (Genetron-23); samples analyzed by gas chromatography (TC) gave only one component, and the mass spectrum was consistent with the formula CF_3H. $NaOD/D_2O$ solutions were prepared by reaction of Na with D_2O. Solutions of Fisher Scientific Certified ACS grade NaF in deionized water, used to calibrate the fluoride ion electrodes, were stored in capped polyethylene bottles.

Deuterium-Exchange Runs. A sketch of the stirred reactor employed for the gas/liquid isotope exchange runs is shown in Figure 1. The basic design is similar to that used by Delmas et al.[11] for D_2/NH_3 exchange runs; however, the use of three separate components—top, bottom, and stirrer shaft—permitted easier construction and access for cleaning. Total reactor volume was 247 and 256 mL for the two complete units constructed. Solution volume was generally 60 mL.

For the kinetic runs the catalyst solution was degassed during a short period of intermittent pumping before the CF_3H was admitted, usually to 0.1 MPa. Stirring speeds above 400 $\text{r}\cdot\text{min}^{-1}$ (measured by a digital phototachometer) were sufficient to ensure efficient gas/liquid mixing, but magnetic coupling could be maintained up to about 1000 revolutions per min with this system when necessary. It was found that the solution temperature was slightly lower than the bath temperature; the correction varied with temperature, ranging from 0.5 °C at 40 °C to 3.0 °C at 80 °C.

Gas-phase kinetic samples were expanded into individual evacuated 1-mL sample tubes as a function of time. Because the observed rate constant for deuterium exchange into CF_3H was independent of gas pressure over the range of interest (see below), the resultant slight decrease in CF_3H pressure during each run was of no consequence. The CF_3H/CF_3D composition of each sample (5–10 per run) was analyzed by mass spectrometry on a CEC 21-614 instrument. Water vapor in the samples was removed in a dry ice/ethanol trap. The *m/e* peaks at 50 ($^{12}CF_2$), 51 ($^{12}CF_2H$), and 52 ($^{12}CF_2D$) were used in the analysis, with a correction of 1.1% ^{13}C made for $^{13}CF_2$ at 51 and $^{13}CF_2H$ at 52. Pseudo-first-order plots of ln (% CF_3H) vs. time were remarkably linear, with correlation coefficients generally 0.998 or more even for cases where there was only 3–5% reaction after 5 h. Data points were usually within 0.1% of the least-squares lines.

The rate constants, k_{obsd}(vap), were shown to be independent of initial gas pressure in the stirred reactor; kinetic results agreed within experimental error of ±10% (no trend) for a set of runs started with 0.100, 0.066, and 0.033 MPa of CF_3H at 67.8 °C and 0.94 $\text{mol}\cdot\text{L}^{-1}$ $NaOD/D_2O$. For this and other cases, multiple runs were often carried out with the same catalyst solution by replacement of the gas charge with fresh stock.

CF_3H Gas Solubility. Solubilities were measured as a function of NaOH concentration and temperature by the gas chromatographic method described previously for H_2 studies.[12,13] Calibration was done with

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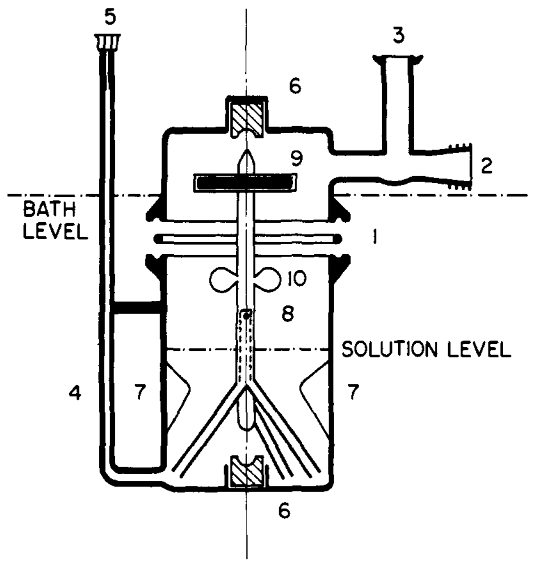

Figure 1. Pyrex gas/liquid stirred reactor (body height 130 mm): (1) 65-mm O-ring joints; (2) greaseless valve; (3) O-ring joint to gas sampling tubes; (4) capillary tube for solution sample withdrawal by syringe through valve at needle 5; (6) Teflon- or polyethylene-bearing surfaces; (7) three baffles; (8) hollow lower shaft to three gas dispersion legs; (9) magnetic stirring bar in glass; (10) two paddles for gas mixing. Stirrer is driven via strong horseshoe magnet attached to variable-speed motor.

a Carle gas sampling valve. Linear response of the TC detector was confirmed over the range of CF_3H sample sizes encountered. CF_3H pressure over each solution was maintained at 0.1 MPa (760 mm) in the equilibrium flask. Several samples, 0.5–1.5 mL each depending on CF_3H solubility, were taken by syringe over a period of at least 2 h until reproducible values were obtained for solubility. The actual amount of solution delivered to the gas stripping cell was determined by change in weight of the syringe.

CF_3H Hydrolysis. Chloroform undergoes hydrolysis at a measurable rate in alkaline solution,[14] but fluoroform has now been found to be fairly resistant to hydrolytic attack. By analogy with Hine's equations for CCl_3H,[14] it was assumed that CF_3H hydrolysis can be represented by the overall equation (1). A fluoride ion-selective electrode (Orion Research

$$2CF_3H + 7NaOH \rightarrow CO + NaHCO_2 + 6NaF + 4H_2O \quad (1)$$

Model 94-09 single unit or 96-09 combination unit) was used with a digital millivolt meter to monitor the increase in [F^-] with time. Solution samples were withdrawn by syringe from the stirred reactor through the capillary side arm. Each run was begun with 60 mL of 1.0 mol·L^{-1} NaOH solution and 0.1 MPa of CF_3H; a ballast volume of 1 L of CF_3H was attached to minimize gas pressure drop.

At each sampling (5–10 per run) about 1 mL of solution was discarded and then 2.5 mL were transferred to a 30-mL polyethylene beaker together with 2.5 mL of H_2SO_4 solution (concentration comparable to that of catalyst) and 5.0 mL of TISAB II Orion prepared buffer solution. Measured F^- concentrations were generally in the range $(1-5) \times 10^{-4}$ mol·L^{-1}.

Results

CF_3H Gas Solubility. In Figure 2 are shown the solubility-temperature profiles for CF_3H in deionized water and 0.99 mol·L^{-1} NaOH solution. Most points fall within 1% of the smooth curves. Each point represents an average of at least three solution samples, with an estimated error of ±2% or less. For pure water at 0.10 MPa of CF_3H pressure the partial molal enthalpy and entropy of solution of CF_3H were determined to be -17 ± 2 kJ·mol^{-1} and -50 ± 6 J·mol·K^{-1}, respectively, in the region 25–35 °C (data treatment according to ref 15).

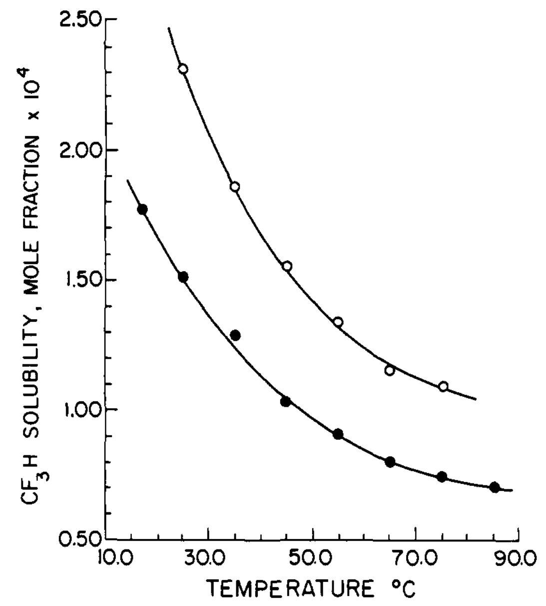

Figure 2. Dependence of CF_3H solubility on temperature for distilled water (○) and 0.99 mol·L^{-1} NaOH (●) (gas pressure 0.1 MPa).

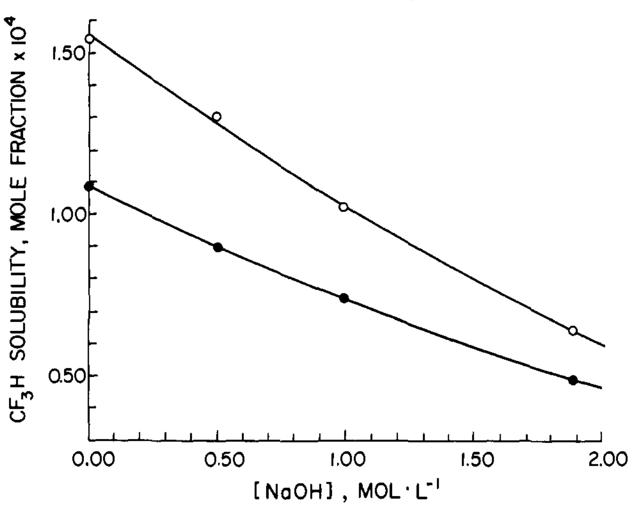

Figure 3. Dependence of CF_3H solubility on NaOH concentration at 45 °C (○) and 75 °C (●) (gas pressure 0.1 MPa).

The dependence of CF_3H solubility on NaOH concentration is given in Figure 3 for 45 and 75 °C. The salting-out effect of the NaOH is quite strong, comparable to that observed by Gubbins et al.[16] for the effect of KOH on CH_4 solubility. For 1.03 mol·L^{-1} salt at 45 °C, the activity coefficients x_1^0/x_1[16] for CH_4/KOH solution and CF_3H/NaOH solution are 1.50[16] and 1.52, respectively.

CF_3H Isotope Exchange. In-solution pseudo-first-order rate constants, k_{obsd} (soln), were obtained by multiplying the experimental k_{obsd} (vap) data by the appropriate conversion factor:[11] (total moles of CF_3H in reaction vessel)/(moles of CF_3H dissolved in catalyst solution). The magnitude of this factor varied with catalyst concentration and temperature and ranged between 25 and 60.

The plot of log k_{obsd}(soln) vs. H_- is shown in Figure 4. The H_- data for NaOH solutions were those of Yagil.[17] Although there is some scatter, the dependence on H_- is clearly close to 1.0 over a 20-fold increase in NaOH concentration.

The Arrhenius activation energy was determined over the temperature range 49–77 °C. The value of E_a from the slope of the line in Figure 5 is a fairly high[4] 134 ± 7 kJ·mol^{-1} (32.0 ± 1.6 kcal·mol^{-1}). $\Delta S^{\ddagger}$, calculated via the equation given by Bunnett[18] using second-order rate constants, is $+75 \pm 21$ J·mol^{-1}·K^{-1} ($+18 \pm 5$ cal·mol^{-1}·K^{-1}); $\Delta G^{\ddagger}$ is 107 kJ·mol^{-1}.

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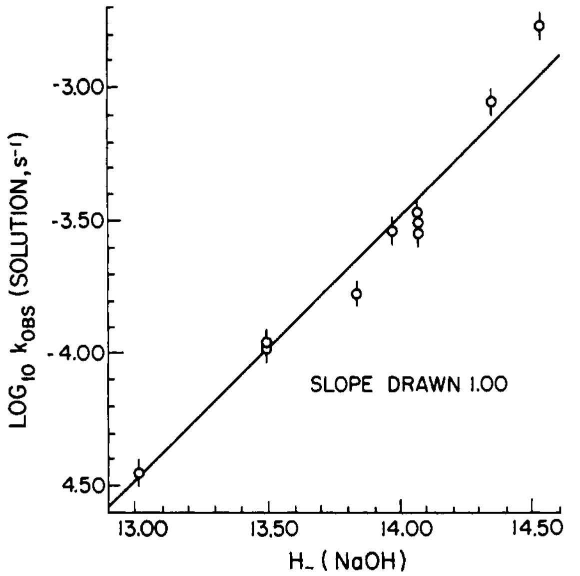

Figure 4. Dependence of CF_3H-exchange rate constant on catalyst solution basicity at 67.8 °C. Error bars represent ±10%.

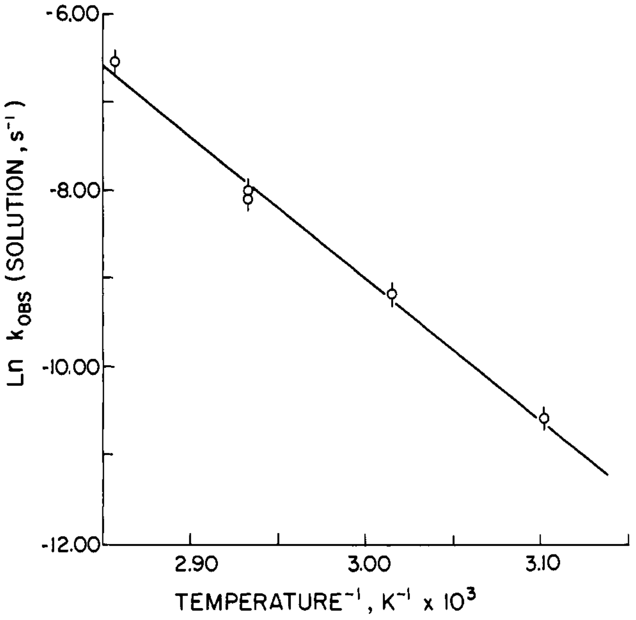

Figure 5. Arrhenius plot for CF_3H exchange in 0.94 mol·L^{-1} NaOD/D_2O at 49–77 °C. Error bars represent ±10%.

CF_3H Hydrolysis. The formation of F^- was very slow—typically a few percent reaction after several days at 60–80 °C—so that only initial rate plots could be made. There was considerable scatter in the data, but plots of {CF_3H solubility—([F^-]/3)} (3 mol of F^- formed/1 mol of CF_3H lost, eq 1) were reasonably linear. However, the initial rate data showed poor reproducibility between runs and only a small temperature dependence. Replacement of the Teflon bearings in the stirred reactor with polyethylene units did not lead to a significant change in rate of F^- formation from a fresh solution, so it would appear that alkaline attack on the Teflon was not producing the observed F^-.

Because of the slow hydrolysis reaction, very low concentrations of the other products were expected (cf. eq 1), and no attempt was made to identify them. The measured initial rates of CF_3H loss were in the range (1–5) × 10^{-10} mol·L^{-1}·s^{-1} at 59–77 °C, which puts hydrolysis about a factor of 10^4 slower than isotope exchange under comparable conditions.

Discussion

CF_3H Gas Solubility. There are only very limited data in the literature for CF_3H solubility in water. One reported value[19] is 0.10 wt % at 25 °C and 0.1 MPa of pressure, which is equal to 2.6 × 10^{-4} mole fraction. It seems likely this was taken from the work of Parmelee, who had earlier published[20] solubility data for a series of halocarbons in water as a function of temperature; an estimate from his Figure 11, after conversion of units, is also about 2.6 × 10^{-4} mole fraction. Our value from Figure 2 is 2.31 × 10^{-4} mole fraction at 25 °C.

Repka and Shteinman give the value 1.97 × 10^{-2} mol·L^{-1} for CF_3H (0.1 MPa partial pressure) in water at 20 °C;[6] this becomes 3.55 × 10^{-4} mole fraction. From extrapolation of Figure 2, our value is 2.60 × 10^{-4} mole fraction.

CF_3H Isotope Exchange—Comparison with Other Haloforms. Slaugh and Bergman reported negligible exchange for CF_3H shaken with 1.1 mol·L^{-1} NaOH/D_2O solution at 15–25 °C.[5] An extrapolation of the least-squares straight line in Figure 5 to 25 and 15 °C gives estimates of the in-solution exchange half-life of 7.6 and 50 h, respectively, for 1 mol·L^{-1} catalyst. The authors do not indicate the size of their reaction vessel, but an assumption of 1 L leads to a predicted *vapor-phase* half-life in their system of the order of 460 h at 25 °C and 3000 h at 15 °C. They detected <0.05% exchange after 1121 h, which is not inconsistent with the above prediction, considering the uncertainty in extrapolation and vessel volume.

Gordy et al.[21] had earlier observed partial conversion of CF_3H to CF_3D in a potassium carbonate/D_2O solution heated to 120 °C for 8 days. It is clear from Figure 5 that, because E_a is so large, reaction at, e.g., 100 °C, should be quite fast, with $t_{1/2} \approx$ 30 s predicted for 1 mol·L^{-1} NaOD/D_2O solution. In fact, we have been able to prepare 97.6 mol % CF_3D in one step at 105 °C; experimental details are given in paper 2.[10]

The activation parameters in the Results for CF_3H (49–77 °C region) can be compared with the data from Hine et al.[4] for hydroxide ion catalyzed exchange in the corresponding Cl, Br, and I deuteriotrihalomethanes (0–35 °C): CF_3H, $\Delta H^\ddagger$ = 131 kJ·mol^{-1}, $\Delta S^\ddagger$ = 75 J·mol^{-1}·K^{-1}; CCl_3D, 98, 72; CBr_3D, 85, 63; CI_3D, 85, 61. There is a strong correlation between increasing exchange reactivity and decreasing $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values. Several authors have discussed the various factors which contribute to the relative ability to fluorine and the other halogen atoms to affect C–H bond acidity.[4,22,23] Our results for CF_3H complement those published for the more reactive haloforms in this series.

CF_3H Isotope Exchange—Water vs. Methanol. Andreades[7] reported results for fluoroform exchange with methanol under methoxide ion catalysis. NaOMe/MeOH is a more basic system than NaOH/H_2O (based on the H_- values for 0.21 mol·L^{-1} solutions, which are 16.18[24] and 13.33[25], respectively). However, while k_{obsd} for CF_3D exchange in NaOH solution is 5.4 × 10^{-5} s^{-1} at 70 °C, Andreades' value[7] for the corresponding NaOMe solution is 1.1 × 10^{-6} s^{-1}, which is a factor of ca. 50× *slower*. He had studied deuterium exchange for a series of monohydrofluorocarbon acids, via a sealed tube kinetics procedure for the gaseous compounds; there was no continuous gas/liquid agitation, only a brief mixing at the start of each run. Also, it was apparently assumed that all the gas in each tube was in solution: [CF_3H] was given in Table I[7] as 0.81 mol·L^{-1}. We have estimated its solubility in 0.21 mol·L^{-1} NaOMe/MeOH solution at 70 °C to be 0.083 mol·L^{-1}, with 0.1 MPa of gas pressure maintained over the solution (extrapolated from data measured at 0.042 and 0.080 MPa of pressure). Thus the difference between the water and methanol results could arise from a lack of gas/liquid mixing in the methanol system, from a failure to correct for gas distribution between the liquid and vapor phases in each tube or from a true

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Table I. Estimate of Trihalomethane pK_a's, Based on Hydrogen Isotope Exchange Reactivity in NaOH/H_2O Solution Relative to CF_3D (pK_a = 27, See Text)

substd methane	$10^4 k_2$ at 0 °C,[a] L·mol^{-1}·s^{-1}	estd pK_a (Streitweiser)[b]		lit. values
CF_3D	1.8×10^{-5} [c]	27[d]	27[e]	26[27]
CCl_2FD	0.89	18	23	
CBrClFD	21	15	21	
CCl_3D	47	15	21	15,[27] 15.5[29] 20,[30] 24[8]
CBr_2FD	180	13	20	
CCl_2ID	275	13	20	
CCl_2BrD	290	13	20	
$CClBr_2D$	1435	12	19	
CBr_3D	5790	11	18	9,[27] 13.7[29]
CI_3D	6010	11	18	13.7[29]

[a] Data from ref 4, except CF_3D; $k_2 = k_{obsd}(soln)/[^-OH]$. [b] ±1 unit. [c] Estimated from CF_3H data at higher temperature, via E_a and (CF_3D, NaOH/H_2O), (CF_3H, NaOD/D_2O) exchange at 68 °C. [d] Set based on log k/pK_a slope of −0.52 (cf. fluorohydrocarbon acids, ref 28). [e] Preferred set based on log k/pK_a slope of −1.0 (cf. ref 8 and 10).

higher catalytic reactivity of the hydroxide/water solution for this reaction.

In an attempt to determine the source of the above difference, CF_3D was contacted with 0.21 and 1.05 mol·L^{-1} NaOMe/MeOH solutions at 70.0 °C in our stirred reactor. It was found that the in-solution rate constants were in fact quite small and that within an experimental error of ±10% the rate of change of CF_3D/CF_3H composition in the vapor phase was independent of stirring (0 and 500 r·min^{-1} in separate runs). The k_{obsd}(soln) values were 1.9×10^{-6} and 3.1×10^{-5} s^{-1}, respectively, for the two catalyst concentrations. The log of the increase in k_{obsd}, 1.21, compares favorably with the H_- increase, 1.14[24]

It is difficult to make a direct comparison with Andreades' data since the exact experimental conditions for his fluoroform runs are not indicated;[7] the need for a vapor/solution correction factor on his rate constants is not clear from the described analytical method. However, CF_3D exchange in water is definitely a factor of 25× or more *faster* than in methanol instead of ca. 700× *slower* as expected from the relative H_- values for the two 0.21 mol·L^{-1} solutions. The reason may lie in the anticipated higher degree of ion pairing in methanol.[26]

pK_a's of CF_3H and Other Halomethanes. One value published for the pK_a of CF_3H, 26, was obtained from polarographic measurements in anhydrous dimethylformamide for a large series of weak hydrocarbon acids.[27] The only other available value, 28 (Streitwieser scale),[23,27,28] was based on Andreades' rate constant data for exchange of CF_3H in methoxide/methanol solution. A replot (log relative rate vs. pK_a (Streitwieser scale)) of the data in Table IX of ref 28, with our in-solution rate constant for CF_3D exchange, leads to only a small reduction in the latter pK_a value, from 28 to 27.

The above value of 27 for the pK_a of CF_3H, together with an estimate for the CF_3D exchange rate constant in H_2O at 0 °C, was used with the rate constant data reported by Hine et al.[4] for hydroxide ion catalyzed exchange of a series of more reactive deuteriotrihalomethanes in water at 0 °C to predict pK_a values for this series. The results of this log (relative reactivity)–pK_a correlation are given in Table I for two possible slopes for such a correlation: 0.52, as used with the fluorohydrocarbons,[28] and 1.0, which should be more suitable for the localized carbanions[30] associated with trihalomethanes like chloroform[8] and fluoroform.[10] Because the activation energies for isotope exchange vary considerably within this series (134 kJ·mol^{-1} for CF_3H to 85 kJ·mol^{-1} for CI_3D[4]), these "relative" pK_a values will be somewhat dependent on temperature. Available literature data are added for comparison. Although the "0.52" set includes values of 15 and 11 for CCl_3H and CBr_3H, respectively, that agree well with some of the literature data, it seems improbable that their pK_a's can in fact be less than 17 in water.[31] Therefore, the "1.0" set is to be preferred; here there is agreement with the two other values for chloroform, 21 vs. 20[30] and 24.[8]

What is the explanation for the improbably low literature pK_a values noted in Table I for CCl_3H and CBr_3H? One pair was determined by a polarographic method in dimethylformamide,[27] and the others were determined via relative exchange reactivities in 50:50 mol % dimethyl sulfoxide/methanol.[29] The polarographic value of 26 for CF_3H is quite reasonable, but it would appear that the acidities determined in this solvent are overestimated by an increasing amount with increasing acidity *relative to the scale in water.* It is well-known that carbon acidities are often dependent on the medium.[28] On the other hand, the relative exchange reactivity data[29] had been given the "0.52" slope treatment (see Discussion and Table I) and so not surprisingly also predicted the value of about 15 for pK_a (CCl_3H).

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(31) The following tests were done with chloroform and bromoform: 8-mL samples of liquid haloform were mixed at 20 °C for 10 min with 90 mL of deionized water and with 90 mL of 1.0 mol·L^{-1} NaOH/H_2O solution (H_2O pK_a 15.7[28]). For CCl_3H there was a negligible difference in the volumes of the organic layers remaining in contact with the aqueous layers. Essentially no CCl_3H was ionized, so pK_a (CCl_3H) must be >17. For CBr_3H there was again a negligible difference in the volumes of the organic layers under the two test conditions. However, for the NaOH case flakes of a white solid had appeared at the aqueous/organic interface. Within several minutes gas bubbles formed on the surface of the flakes, and the latter finally disintegrated. The white solid was probably CBr_3Na, which was then slowly hydrolyzed in contact with the aqueous layer to produce CO gas. These observations indicate that the pK_a of CBr_3H is greater than 15.7 by at least one pK_a unit.