

## Deuterium-Exchange Reaction on Trimethylamine–Borane with Sulfonate Cation Exchanger in the Deuterio Form

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The kinetics of H–D exchange on trimethylamino–borane in bi- and triphase systems involving sulfonate cation exchangers in the D<sup>+</sup> form show that the rate of the isotope exchange is lower in triphase systems in comparison to the liquid–liquid extraction system; nevertheless the yield of the deuterated product in polymeric deuterating systems is essentially much higher than that obtained in applying liquid deuterating agents. The cation-exchange resin when applied in triphase system demonstrates ambivalent behavior, acting as a catalyst toward deuterio-exchange reaction and as a suppressor toward the hydrolysis of TMAB. The hydrolysis of TMAB results in the formation of trimethylamine which accelerates the hydrolysis and inhibits the H–D exchange by saturation of the SO<sub>3</sub><sup>-</sup> resin sites. The immobilization of the aqueous phase (D<sub>2</sub>O) in swollen ion exchanger creates unique conditions for isotope exchange, completely suppressing hydrolytic side reactions, and pure deuterated product can be achieved in quantitative yield.

### Introduction

Trialkylamine–boranes have been known since 1937<sup>1–3</sup> and are widely used as selective reducing and hydroborating agents in organic synthesis<sup>4–6</sup> and for metal reduction (see, e.g., refs 7–9). Deuterated trialkylamine–boranes and trimethylamine–borane (TMAB) in particular are the most important intermediates for the synthesis of alkali metal borodeuterides, effectively employed for selective introduction of deuterium into organic compounds containing reducible functional groups. A particular interest in monoisotopic forms of alkali metal borohydrides (e.g., tritium-free NaBH<sub>4</sub>) has arisen recently and is connected with solar neutrino experiments, where this compound is applied for reducing GeCl<sub>4</sub> into GeH<sub>4</sub>.<sup>10,11</sup> Deuterated borohydrides are also suggested to be appropriate candidates for this purpose.

The hydrogen–deuterium exchange of boron-bound hydrogens in TMAB was originated by Davis et al.<sup>12</sup> and later reinvestigated (in a scaled-up process) by Atkinson et al.<sup>13,14</sup> The isotope-exchange reaction on TMAB<sup>14</sup> is carried out in the liquid–liquid extraction system by consequential treatment of an etheric TMAB solution by consecutive portions of D<sub>2</sub>SO<sub>4</sub> (10 times!) and is based on the exchange interaction of boron hydride hydrogens with deuterons.<sup>15</sup> In the case of TMAB this interaction is known to be accompanied by rather intensive hydrolysis<sup>12–14</sup> that releases hydrogen (or HD), boric acid, and trimethylamine.<sup>16,17</sup> A detailed investigation of the kinetics of TMAB hydrolysis has been carried out by Ryschkewitsch<sup>16</sup> and Davis.<sup>17</sup> Nevertheless, none of the publications describing deuteration of TMAB report any quantitative data on the rates of the isotope-exchange reaction or that of the accompanying hydrolysis reaction, although information of this type is available in some publications concerning deuteration of boranes.<sup>18–23</sup> Nonetheless, an overall kinetic mechanism has not been presented until now.

The aims of the present study were as follows: (1) Develop a new principle for carrying out the hydrogen–deuterium exchange reaction on a solid polymeric deuterating agent, namely, sulfonate cation exchanger in the D<sup>+</sup> form. (2) Investigate the kinetics of H–D exchange in bi- and triphase systems consisting of liquid and solid deuterating agents. (3) Attempts to elucidate the kinetic mechanism of H–D exchange for deuterating ion-exchange resins.

### Experimental Section

**Materials.** Trimethylamine–borane was synthesized and purified as described elsewhere.<sup>24a</sup> Deuteriosulfuric acid (98%), deuterium oxide (99.9%), sodium borodeuteride (98% atom D), carbon tetrachloride (A.R. grade), trimethylamine hydrochloride (98%), and chloroform-*d*<sub>3</sub> were all obtained from Aldrich Co. and used as received. Solutions of HCl and NaOH were prepared from Merck standard solutions. Samples of granulated sulfonate cation-exchange resins, Dowex 50×2 (40–60 mesh) and Dowex 50×8 (200–400 mesh), were transformed into the deuterio form according to the following procedure.

A portion of the cation exchange resin was placed into the column and subsequently treated with 0.5 M solutions of NaCl and HCl. After transformation of the ion exchanger into H<sup>+</sup> form, the resin was rinsed with deionized water and then treated with a 0.5 M solution of LiOH. The resin in Li<sup>+</sup> form was washed with deionized water and then separated from the aqueous phase by filtration. The resin was treated with 95% ethanol to extract most of the water from the swollen resin beads. The final elimination of the remaining water was carried out by washing with absolute ethanol. Then the beads were dried in the oven at 100 °C under vacuum for 72 h till constant weight was reached.<sup>28</sup> A dry sample of the ion exchanger was placed in D<sub>2</sub>O to swell and then treated in a column with 1.0 mol/dm<sup>3</sup> solution of D<sub>2</sub>SO<sub>4</sub> in D<sub>2</sub>O. Completion of lithium to deuterium displacement was controlled by flame photometry. Excess D<sub>2</sub>SO<sub>4</sub> from the interbed (and adsorbed acid) were removed by rinsing the resin phase with several portions of D<sub>2</sub>O to neutral reaction.

The concentration of H<sup>+</sup>, D<sup>+</sup>, and OH<sup>-</sup> ions in aquatic phase were determined by potentiometric titration using a Corning Model 240 pH meter supplied with a combined glass electrode. A Nicolet 510 FTIR spectrometer was used to record infrared spectra in the range 4000–400 cm<sup>-1</sup>. The IR spectra were run in a standard NaCl cell. The <sup>1</sup>H and <sup>11</sup>B NMR spectra were recorded using a Bruker AMX400 spectrometer (proton resonance at 400.13 MHz and <sup>11</sup>B resonance at 128.38 MHz) using a tip angle of 90° and a pulse repetition time of 1 s (for details see ref 24b). The concentration of Li<sup>+</sup> ions was determined by absorption photometry using a Varian Techtron Atom Absorption photometer (The equilibrium constant of Li<sup>+</sup>–H<sup>+</sup> exchange is most favorable and is close to unity.<sup>25–27</sup> (The equality of Li → H vs Li → D exchange is assumed).)

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TABLE 1: System Parameters<sup>a</sup>

system no.	no. of phases	type of phase	aqueous phase	solid phase	reaction studied	remarks
S <sub>1</sub>	2	L/L	1.6 M D <sub>2</sub> SO <sub>4</sub> in D <sub>2</sub> O		H-D exchange	hydrolysis of TMAB was observed but not measured quantitatively
S <sub>2</sub>	3	L/L/S	D <sub>2</sub> O pD ≈ 6	Dowex 50×2	H-D exchange hydrolysis	resin granulation 40–60 mesh
S <sub>3</sub>	3	L/L/S	D <sub>2</sub> O pD ≈ 6	Dowex 50×8	H-D exchange hydrolysis	resin granulation 200–400 mesh
S <sub>4</sub>	2	L/-/S	-	Dowex 50×2	H-D exchange	resin granulation 40–60 mesh; resin phase was preliminarily swollen in D <sub>2</sub> O and washed from the sorbed D <sub>2</sub> SO <sub>4</sub>
S <sub>5</sub>	2	L/-/S	-	Dowex 50×2	H-D exchange hydrolysis	resin granulation 40–60 mesh; sorbed D <sub>2</sub> SO <sub>4</sub> was not removed from resin phase
S <sub>6</sub>	3	L/L/S	0.14 M TMA in D <sub>2</sub> SO <sub>4</sub> pD ≈ 6	Dowex 50×2	H-D exchange hydrolysis	resin granulation 40–60 mesh

<sup>a</sup> pD = -log[D<sup>+</sup>]; TMA = trimethylamine; TMAB = trimethylamine-borane. Organic phase (1): 15 mL of 0.1 M TMAB in CCl<sub>4</sub>. Solid phase (3): 2.5 mequiv of SO<sub>3</sub>-D<sup>+</sup> groups. Types of phases: L, liquid; S, solid; -, none.

## Methods

The kinetic experiments were carried out using the limited volume method (ref 29, p 309) (batch conditions), according to the following technique: 15 mL of 0.1 mol/dm<sup>3</sup> solution of TMAB in CCl<sub>4</sub> (1.5 mmol); 15 mL of the respective aqueous phase and the known amount of ion exchanger (2.50 mequiv in the swollen state) were placed in a reaction vessel connected to a calibrated gasometric tube and stirred vigorously by propeller at 22 ± 1 °C in a temperature-controlled laboratory. The time of acid addition (liquid or solid) was counted as zero time. The phase contact time varied from several minutes to several hours. After a given period of time stirring was stopped, and 40 μL of the organic phase was withdrawn for IR analysis. Stirring was then resumed. The rate of isotope exchange was monitored following the disappearance of the strong 2360-cm<sup>-1</sup> absorption band (B-H bond) and appearance of a broad 1783-cm<sup>-1</sup> (B-D bond) band. The hydrolysis process was followed by both IR analysis and volumetric measurements of the gas evolving the reactor. For a quantitative interpretation, calibration curves based on the integral intensities of absorption bands characterizing B-D and B-H bonds were prepared using standard solutions of TMAB and TMAB-d<sub>3</sub>. TMAB-d<sub>3</sub> was synthesized from sodium borodeuteride and trimethylamine hydrochloride according to the procedure described elsewhere.<sup>30</sup>

## Results

The main parameters of the systems (S<sub>1</sub> to S<sub>6</sub>) under investigation are presented in Table 1. S<sub>1</sub> is similar to the liquid-liquid biphasic system studied by Davis or Atkinson, except that the solvent was changed from ether to CCl<sub>4</sub>. Systems S<sub>2</sub> and S<sub>3</sub> are triphasic systems in which the cation-exchange resin Dowex-50, carrying 20 times less amounts (than in the case of S<sub>1</sub>) of sulfonic acid groups (2.5 mequiv), was employed. The difference between S<sub>2</sub> and S<sub>3</sub> is in cross-linking density (2% DVB in S<sub>2</sub>, 8% DVB in S<sub>3</sub>) and resin granulation (40–60 mesh in S<sub>2</sub>, 200–400 mesh in S<sub>3</sub>). Systems S<sub>4</sub> and S<sub>5</sub> are attempts to eliminate the aqueous phase as a source of deuterons and use only the SO<sub>3</sub>-D<sup>+</sup> groups of the resin and D<sub>2</sub>O uptaken by the swollen ion exchanger. They are the biphasic analogs of S<sub>2</sub>. The difference between S<sub>4</sub> and S<sub>5</sub> is that in S<sub>4</sub> the sorbed D<sub>2</sub>SO<sub>4</sub> was carefully removed by D<sub>2</sub>O washings.

System S<sub>6</sub> is a conclusive experiment aimed at presenting the effect of trimethylamine (TMA) on both hydrolysis and H-D exchange reactions.

Progress of the H-D reaction was followed by FTIR of the organic phase, following the BH<sub>3</sub> and BD<sub>3</sub> antisymmetric stretches at 2360 and 1780 cm<sup>-1</sup>, respectively (see Figure 1).<sup>31,32</sup>

The quantitative expression in terms of TMAB and TMAB-d<sub>3</sub> concentrations of the data presented in Figure 1 was achieved by aid of calibration curves as shown in Figure 2. Figure 2a shows the linear calibration curves (in the range of concentrations studied) for TMAB solutions obtained by integrating either one

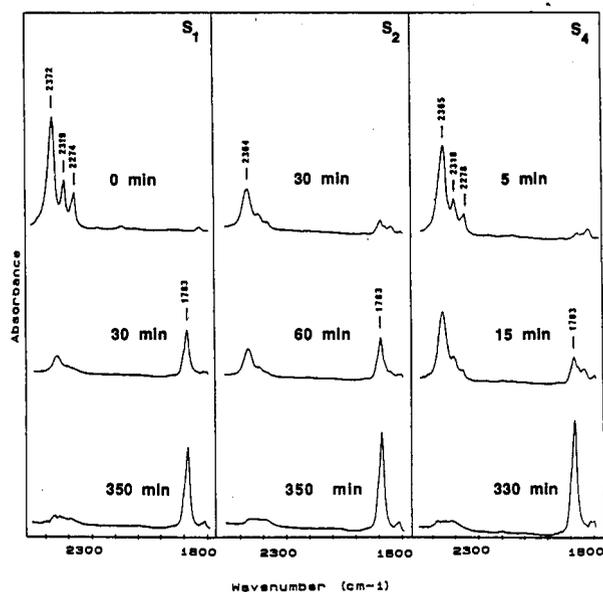


Figure 1. Typical FTIR spectra of organic phase containing TMAB at increasing time intervals for systems S<sub>1</sub>, S<sub>2</sub>, and S<sub>4</sub> (see Table 1). Sampling time (in minutes) is indicated.

band (curve A) at a frequency of 2372 cm<sup>-1</sup> or three bands at frequencies of 2372, 2318, and 2273 cm<sup>-1</sup> (curve B). Curve B provided a more accurate determination of TMAB concentration and was used for quantitative treatment of FTIR data. Comparison of the spectra shown in Figure 1 demonstrates that the deuterated product is formed in higher concentration in systems 2 and 4 than in system 1.

From the concentrations of TMAB and TMAB-d<sub>3</sub> the conversion degrees ( $F_e$ ) were calculated as follows:

$$F_e = C_t/C_0, \quad 0 \leq F_e \leq 1 \quad (1)$$

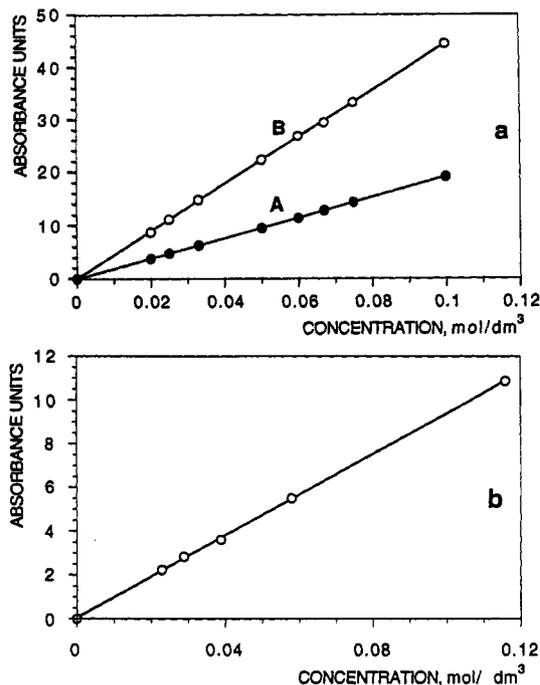
where  $C_0$  is the initial concentration of TMAB (0.1 mol/cm<sup>3</sup>) and  $C_t$  is the concentration of TMAB-d<sub>3</sub> observed at a moment  $t$ , in mol/dm<sup>3</sup>.

The degree of hydrolysis of TMAB and TMAB-d<sub>3</sub> ( $F_H$ ) was calculated from the results of the volumetric analysis as follows:

$$F_H = V_t/V_{\max}, \quad 0 \leq F_H \leq 1 \quad (2)$$

where  $V_t$  is the volume of hydrogen (or HD) evolved at time  $t$ , cm<sup>3</sup>,  $V_{\max}$  = 110.8 cm<sup>3</sup> is the maximum volume of hydrogen evolved by complete hydrolysis of 1.5 mmol TMAB.<sup>24c</sup> Kinetic data for both deuteration and hydrolysis processes are presented as plots of respective  $F$  values versus time. The relative errors of  $F_e$  and  $F_H$  determination did not exceed 7%.

The experiments with system 1 (0.1 M TMAB in CCl<sub>4</sub>-1.6 M D<sub>2</sub>SO<sub>4</sub> in D<sub>2</sub>O) were carried out according to the published technique<sup>13,14</sup> but under more favorable conditions for isotope exchange (higher concentration of D<sub>2</sub>SO<sub>4</sub>) to achieve complete



**Figure 2.** Calibration curves for FTIR spectra of carbon tetrachloride solutions of TMAB (a) and TMAB- $d_3$  (b). In Figure 2a, the integration of three bands at frequencies of 2372, 2318, and 2273  $\text{cm}^{-1}$  (curve A) and of one band at frequency of 2372  $\text{cm}^{-1}$  (curve B) is shown.

**TABLE 2: Main Parameters of TMAB Deuteration Process in Applying Liquid and Solid Deuterating Agents<sup>a</sup>**

system no. (see Table 1)	no. of phase	type of phase	time of half-conversion ( $t_{0.5}$ ) min	max concn of TMAB- $d_3$ , observed, mol/dm <sup>3</sup>	degree of TMAB hydrolysis observed in $t_{0.5}$ , %
S <sub>1</sub>	2	L/L	23	0.070	15
S <sub>2</sub>	3	L/L/S	81	0.088	9
S <sub>3</sub>	3	L/L/S	63	0.081	7
S <sub>4</sub>	2	L/-/S	45	0.100	<1
S <sub>5</sub>	2	L/-/S	28	0.075	13
S <sub>6</sub>	3	L/L/S	670	0.083	13

<sup>a</sup> Types of phases: L, liquid; S, solid; -, none.

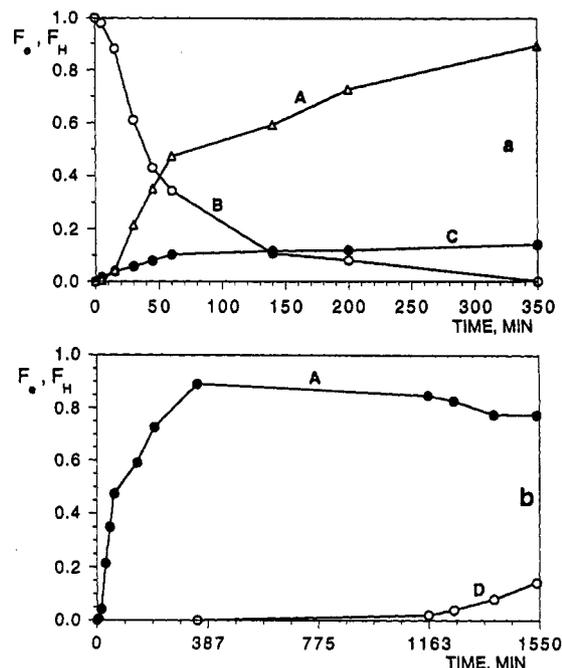
conversion of TMAB into the deuterated product in one stage. (See appendix, Figure 9. In this series of experiments an intensive release of a gas was observed, but the hydrolysis was not measured quantitatively.) It follows from the data shown in Figure 9 (Appendix) that the rate of deuteration (see curve A) is fast but vigorous contact of TMAB with the acidic aqueous phase promotes hydrolysis and decreases yields of TMAB- $d_3$ .

The analysis of the results obtained in the six systems studied must first be viewed in a practical way, and second in a theoretical mechanistic way. Table 2 presents<sup>3</sup> the main parameters of the TMAB deuteration processes, namely, the time ( $t_{0.5}$ ) for half-conversion; the maximum concentration of TMAB- $d_3$  product obtained and a degree of unwanted hydrolysis of TMAB. No doubt, the biphasic system,  $s_4$ , is the practically optimal system, providing maximum concentration of TMAB- $d_3$  (0.100 mol dm<sup>-3</sup>), and less than 1% hydrolysis at  $t_{0.5} = 45$  min.

The kinetic data generated for systems S<sub>1</sub>-S<sub>6</sub> are most illuminative and worthy of careful presentation. Yet, for the sake of brevity and clearness, we are presenting only selected results.

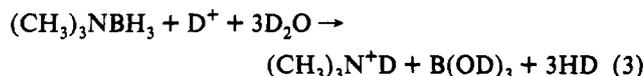
On examination of system S<sub>2</sub> (0.1 M TMAB in CCl<sub>4</sub> as phase L<sub>1</sub>; D<sub>2</sub>O at pD = 6 as L<sub>2</sub> and Dowex 50×2 in D<sup>+</sup> form as phase S), it is possible to note the following processes taking place.

(1) **Hydrolysis**  $0 < t < 5$  min. Rather fast primary hydrolytic decomposition of the initial TMAB proceeds according to the

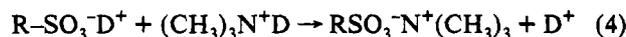


**Figure 3.** Kinetics of H-D exchange (curves A and B) and hydrolysis of TMAB-TMAB- $d_3$  mixture (curve C) and of pure TMAB- $d_3$  (curve D) in presence of Dowex 50×2 in D<sup>+</sup> form in triphase system (system 2). Kinetic curves are shown for time intervals: 350 min (a), 1550 min (b), corresponding to BD<sub>3</sub> conversion (curve A) and to BH<sub>3</sub> conversion (curve B).

following equation:



and promotes the accumulation of trimethylammonium (TMA) ions in the aqueous phase. TMA ions are known to increase the hydrolysis of TMAB<sup>16</sup> possibly by action as a phase-transfer catalyst (see, e.g., refs 34 and 35). On the other hand, they bind to the resin phase and release deuterons:

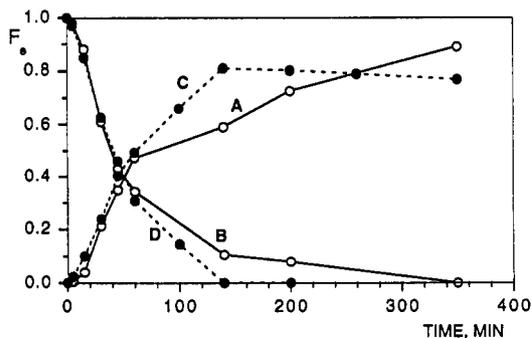


(2) **Isotope Exchange**  $5 < t < 60$  min. The ion-exchange reaction results in simultaneous removal of TMA from the aqueous phase, and in the enrichment of this phase with deuterons. The first process leads to the progressive decrease in the rate of TMAB hydrolysis, and the second enhances the rate of isotope-exchange reaction, now reaching the maximum value.

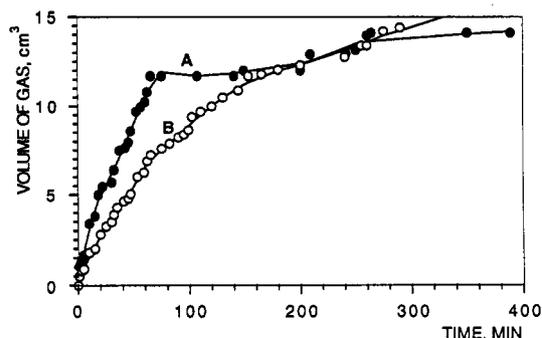
(3) **Inhibition**  $60 < t < 350$  min. Finally, the gradual loading of the cation exchanger with TMA begins inhibiting the ion-exchange process. This inhibition may be explained by the surface activity of TMA ions, which resemble the cationic surfactants, known to slow down the process of ion exchange and even poison resins.<sup>36</sup>

This can be seen from the data given in Figure 3. As follows from parts a and b in Figure 3 (curves A), complete conversion of TMAB to TMAB- $d_3$  is slower than in the case of S<sub>1</sub>. As seen from Figure 3b, the deuterated TMAB is stable and is not readily hydrolyzed. The hydrolysis of TMAB- $d_3$  in this system is characterized by a time lag (see curves C and D) similar to that observed in a membrane version of TMAB deuteration process.<sup>24b</sup> This simplifies operational conditions for the recovery of the product from the reaction mixture with a reasonably high yield.

As seen in Figure 3a, curve A is characterized by three clearly distinguished kinetic steps corresponding to  $0 < t_1 < 15$  min,  $15 < t_2 < 60$  min and  $60 < t_3 < 350$  min time intervals. The first and the third steps are slow and the second is rather fast. Curve C is segmented into two parts, corresponding to the fast and slow



**Figure 4.** Kinetics of TMAB deuteration in triphase systems 2 (curves A and B) and 3 (curves C and D). Curves A and C correspond to  $\text{BD}_3$  conversion; curves B and D correspond to  $\text{BH}_3$  conversion.



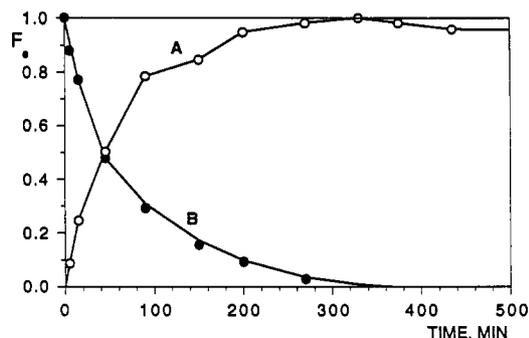
**Figure 5.** Kinetics of gas evolution in system 2 (curve A) and in system 3 (curve B).

kinetic steps of the TMAB hydrolysis, respectively, and besides, the inflection point on the curve C coincides with that on curve A, corresponding to  $t = 60$  min. This indicates that both isotope-exchange and hydrolysis processes are coupled and influence each other, at least in the triphase systems  $S_2$ ,  $S_3$ , and  $S_6$ .

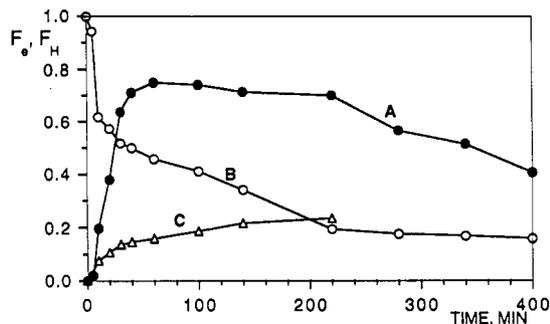
In the case of system 3 (0.1 M TMAB in  $\text{CCl}_4\text{-D}_2\text{O}$ -Dowex 50 $\times$ 8 in  $\text{D}^+$  form) the trends in changing the rates of isotope exchange and hydrolysis reactions follow the same "scenario" as for  $S_3$ , i.e., first the rate of H-D exchange increases, achieving a maximal value and then slows down, while a permanent decreasing rate of hydrolysis is observed.

Moreover, as follows from the data shown in Figure 4, faster isotope exchange is observed in system 3 compared with that in system 2 (cf. curves A and C in Figure 4). At the same time, as seen in Figure 5, the opposite trend can be noticed for the hydrolysis reaction. In the case of system 2, more intensive gas release (curve A) is observed, testifying to more rapid hydrolysis of TMAB in this system.

The kinetic conversion curves in the biphasic reaction mixture [0.1 M TMAB in  $\text{CCl}_4$ -Dowex 50 $\times$ 2 in  $\text{D}^+$  form (40-60 mesh)] (without free deuterium oxide) are presented in Figure 6. During the series of experiments carried out with system 4, gas evolution was not observed; a more detailed investigation of isotope-exchange process in system 4 including the column version of the process in biphasic system (Dowex 50 in  $\text{D}$ -form TMAB solution) in published elsewhere<sup>43</sup> and shows absolute absence of TMAB hydrolysis. The concentration of TMAB- $d_3$  in the organic phase after complete disappearance of the  $\text{BH}_3$  band (FTIR) is equal to the initial concentration of TMAB. The  $^{11}\text{B}$  NMR analysis of the final product (see Appendix Figure 10) demonstrates the formation of spectroscopically pure  $(\text{CH}_3)_3\text{NBD}_3$  complex. This indicates complete suppression of the hydrolytic reaction of both TMAB and TMAB- $d_3$ . As seen from the data shown in Figure 6, the effective rate of isotope-exchange reaction in system 4 is higher than in system 3, despite larger resin bead size (i.e., lower surface area). The shape of the kinetic curve of isotope exchange (curve A in Figure 6) in system 4 differs from that obtained in systems 2 and 3 (cf. curves A in Figures 7 and 3). This signifies

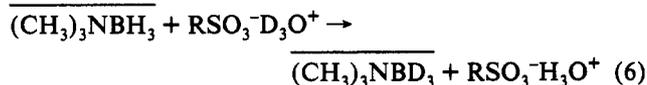
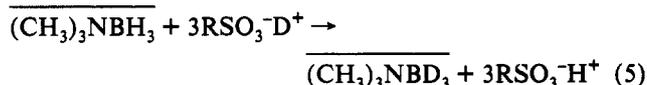


**Figure 6.** Kinetics of H-D exchange on TMAB in biphasic system including Dowex 50 $\times$ 2 in  $\text{D}^+$  form (system 4) correspond to  $\text{BD}_3$  conversion (curve A) and  $\text{BH}_3$  conversion (curve B).

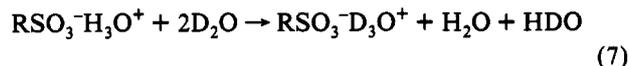


**Figure 7.** Kinetics of H-D exchange (curves A and B) and of hydrolysis of TMAB-TMAB- $d_3$  mixture (curve C) in biphasic system including Dowex 50 $\times$ 2 in  $\text{D}^+$  form with sorbed  $\text{D}_2\text{SO}_4$  (system 5). Curve A corresponds to  $\text{BD}_3$  conversion; curve B corresponds to  $\text{BH}_3$  conversion.

that the mechanism of H-D exchange in system 4 does not involve the kinetic steps described above. This is further supported by the absence of the hydrolysis. The isotope-exchange reaction on TMAB in system 4 can proceed in the resin phase only. This means that in order for the exchange reaction to happen, TMAB must be sorbed by the ion exchanger, as described in the following equations:



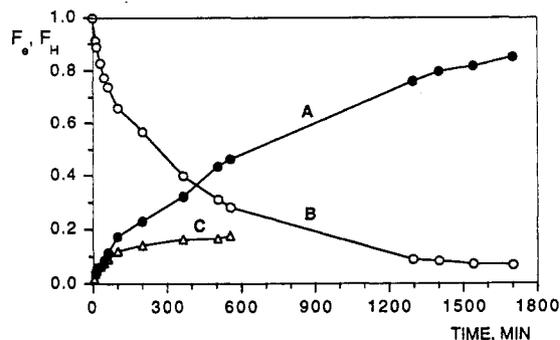
where R denotes the resin phase, and the bar over TMAB indicates its presence in the resin phase. Since the resin phase is a cross-linked ion exchanger preswollen in  $\text{D}_2\text{O}$  it contains a considerable amount of deuterium oxide. This creates the conditions for "self-regeneration" of the exhausted part of the ion exchanger:



We have observed the appearance of  $\text{H}_2\text{O}$  during the H-D exchange on TMAB in our studies on the analogous membrane version of this process.<sup>24b</sup>

As indicated above, the "self-regeneration" of the resin is the key to the success of system 4. Since the preparation of the resin in the  $\text{D}^+$  form involves the use of  $\text{D}_2\text{SO}_4$ , we attempted to understand the influence of sorbed  $\text{D}_2\text{SO}_4$  on the kinetics of both isotope exchange and hydrolysis reactions and so to ascertain whether rinsing the resin after removal of excess  $\text{D}_2\text{SO}_4$  (by filtration) is necessary or not.

The kinetic curves obtained for system 5 [0.1 M TMAB in  $\text{CCl}_4$ -Dowex 50 $\times$ 2 in  $\text{D}^+$ -form (40-60 mesh), without rinsing]



**Figure 8.** Kinetics of H-D exchange (curves A and B) and of hydrolysis of TMAB-TMAB- $d_3$  mixture (curve C) in triphase system including Dowex 50 $\times$ 2 in D $^+$  form and 0.14 M solution of trimethylamine deuteriosulfate in D $_2$ O (system 6). Curve A corresponds to BD $_3$  conversion; curve B corresponds to BH $_3$  conversion.

**TABLE 3: Effective Rates of H-D Exchange ( $R_{IE}$ ) and Hydrolysis of TMAB ( $R_H$ ) in Applying Sulfonate Cation Exchangers in D $^+$  Form as Deuterating Agents**

system (see Table 1)	type of phase	time interval (min)	$R_{IE}$ $\times 10^4$ , s $^{-1}$	$R_H$ $\times 10^4$ , s $^{-1}$	$R_{IE}$ : $R_H$	remarks
S $_2$	L/L/S	0 < $t$ < 5	0.2	0.5	0.4	40-60 mesh
		5 < $t$ < 15	0.7	0.4	1.8	
		215 < $t$ < 60	1.8	0.2	9.0	
		60 < $t$ < 350	0.2	0.02	10.0	
S $_3$	L/L/S	0 < $t$ < 5	0.7	0.3	2.3	200-400 mesh
		5 < $t$ < 15	1.35	0.2	6.8	
		15 < $t$ < 60	1.5	0.2	7.5	
S $_4$	L/-/S	0 < $t$ < 5	2.9			40-60 mesh;
		0 < $t$ < 15	2.7			no D $_2$ O or D $_2$ SO $_4$
S $_6$	L/L/S	0 < $t$ < 15	0.64	0.56	1.1	40-60 mesh
		15 < $t$ < 100	0.23	0.14	1.6	+ TMA
		100 < $t$ < 365	0.09	0.03	3.0	

are shown in Figure 7. The comparison of the data presented in Figure 7 with that shown in Figure 6 allows the conclusion that presence of D $_2$ SO $_4$  in the resin phase significantly intensifies the hydrolytic decomposition of TMAB and decreases the yield of H-D exchange. Thus sorbed acid must be carefully removed from the resin.

Finally, to check the influence of TMA on the kinetics of H-D exchange and on the hydrolysis of TMAB, a series of experiments with system 6 [0.1 M TMAB in CCl $_4$ -0.14 M TMA in D $_2$ O-Dowex 50 $\times$ 2 in D $^+$  form (40-60 mesh)] were carried out. The aqueous phase in these experiments contained 0.14 mol/dm $^3$  TMA, neutralized to pD  $\approx$  6 with a solution of D $_2$ SO $_4$  in D $_2$ O. The kinetic curves obtained are presented in Figure 8. As seen from the data given in Figure 8 with that presented in Figure 3 the presence of TMA in the aqueous phase subsequently slows down the isotope-exchange reaction. Sorption of TMA decreases its concentration in the aqueous phase and slows down the hydrolysis of TMAB. The data obtained for system 6 supports the kinetic mechanism proposed and points to the active role of TMA both in isotope exchange and in hydrolytic processes in triphase systems.

To summarize the comparison, the effective rates of isotope exchange ( $R_{IE} = dF_e/dt$ ) and of hydrolysis ( $R_H = dF_H/dt$ ) are presented for the most interesting systems. Table 3 presents  $R_{IE}$  and  $R_H$  at different reaction time zones. The ratio  $R_{IE}$  to  $R_H$  presents the selectivity of the reaction steps. At the initial time interval (0 <  $t$  < 5 min) the hydrolysis reaction is favored, but this changes with time and higher selectivities for the exchange reaction are obtained after a longer time— $t$  > 5 min for all systems. Exclusion of D $_2$ O or D $_2$ SO $_4$  (system S $_4$ ) ensures almost indefinitely high selectivity for the isotope exchange reaction.

Two other major conclusions are reemphasized. First, that

the granulation (bead size) has an effect on selectivity. Second, that presence of TMA is detrimental.

## Discussion

The meaning of the results of this study may be understood by viewing the major conclusions of Table 3 and relating them to the interactions between phases, giving very similar considerations to that presented by Regen $^{37,38}$  in his classical studies on the triphase system.

First, the biphasic system, S $_1$ , is characterized by exceptionally high yields of hydrolysis. This can now be easily explained because of the constant presence of excess D $_2$ O and D $_2$ SO $_4$  on the liquid interphase of the two phases. Upon elimination of one liquid phase (L $_2$  the D $_2$ O phase), the hydrolysis reaction is completely suppressed, while the isotope-exchange (IE) reaction is not affected. This means that the resin phase acts as a catalyst for the IE reaction (system S $_4$ ). Comparison of triphase systems provides real comparison between the catalytic activity of the resins themselves, since the liquid-liquid interphases may be considered equal for all systems and independent of the resin.

If the surface areas of the resins in S $_2$  and S $_3$  are compared (see Appendix), the ratio is S $_3$ :S $_2$  = 3.5, and so is the ratio of effective IE rates for both systems (see Table 3) at the final time ( $t \geq 60$  min), when the H-D exchange process is considered to be at a steady state. This indicates that the aqueous phase takes minimal or no part in the H-D exchange process. Hence, the aqueous phase may be (theoretically) eliminated. This was confirmed experimentally in system 4. This is a manifestation of a state where the water is actually immobilized in the swollen polymer, in contrast to an organic solution of the reactant. This state should be compared to that of solvent-impregnated resin (SIR), which were studied by us. $^{39-42}$  In the SIR concept, the organic part of the liquid-liquid extraction system is immobilized in a solid phase and thus provides certain advantages in carrying out the liquid-liquid extraction process, mainly the ease of separation of the organic phase (now in solid form) from the aqueous metal-bearing phase.

In this paper, we have demonstrated that immobilization of the aqueous phase provides an advantage for protection from competing hydrolytic reactions.

These conclusions are very important and should be extended to other organic reactions in swollen-solid ion-exchange phases, and we intend to follow this further.

If a comparison is drawn with membrane-assisted reactions, $^{24b}$  the value of the effective rate of H-D exchange would be (1.5-7.5)  $\times 10^{-6}$  s $^{-1}$ , while the surface area (operating areas) would be 3.14 cm $^2$ . $^{24b}$  In system 4, the effective rate for H-D exchange is 2.9  $\times 10^{-4}$  s $^{-1}$ , while the surface area is  $\sim 3 \times 10^2$  cm $^2$ . Hence, the two systems show similar intrinsic rates of exchange.

The other systems involving polymeric deuterating agents also demonstrate higher yields of TMAB- $d_3$  and lower degrees of TMAB hydrolysis than that obtained in applying D $_2$ SO $_4$  (system 1). Published methods of converting TMAB into TMAB- $d_3$  (see, e.g., refs 13 and 14) are based on multistage long-term extraction treatment (10 stages, 24 h each $^{14}$ ) of the initial TMAB by solution of D $_2$ SO $_4$  in D $_2$ O. From the results of the present study, it follows that the conclusions obtained by Atkinson et al. $^{13,14}$  that the yield of (CH $_3$ ) $_3$ NBD $_3$  in applying an extraction technique could reach 60-65% seems dubious, since subsequent repetition of direct contact of TMAB with fresh portions of D $_2$ SO $_4$  during  $\sim 240$  h must result in a high degree of TMAB hydrolysis.

Furthermore, if in the case of liquid-liquid extraction the exhausted solution of the deuterating agent cannot be regenerated and must be replaced with a fresh one after every stage, for instance, when applying polymeric deuteriosulfuric acid the depleted polymer can be reused after the respective regeneration cycle. For example, H $_2$ O and HDO admixtures (appearing in the resin phase according to reaction 7) can be easily removed

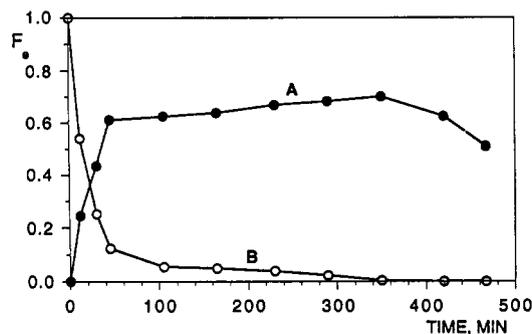


Figure 9. Kinetics of H-D exchange of TMAB in presence of 1.6 M  $D_2SO_4$  in biphasic system (system 1). Curve A corresponds to  $BD_3$  conversion; curve B corresponds to  $BH_3$  conversion.

either by rinsing the resin in a column with  $D_2O$  or by subsequent drying of the resin and placing it in pure  $D_2O$  to swell.

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### Appendix

A. The number of resin beads ( $N_b$ ) in each sample is equal to

$$N_b = 3m/4\pi r_d^3 \rho \quad (8)$$

where  $m$  is the mass of the resin sample (grams),  $r_d$  is the average radius of the dry beads (centimeters), and  $\rho$  is the density of the dry ion exchange ( $g/cm^3$ ).  $m$  and  $\rho$  values are approximately the same for both resin samples;  $N_b$  values differ from each other because of the difference in  $r_d$  values. The surface area ( $S$ ) of a given resin sample in the swollen state is equal to

$$S = 4\pi N_b r_{sw}^2 \quad (9)$$

where  $r_{sw}$  is the average radius of swollen beads (centimeters). Since

$$r_{sw} = r_d K_{sw} \quad (10)$$

where  $K_{sw}$  is the linear swelling coefficient, known to depend on resin cross-linkage. Finally one obtains

$$S = 3m K_{sw}^2 / r_d \rho \quad (11)$$

and the ratio of the surface areas is equal to

$$S_3:S_2 = \frac{K_{sw3}^2 r_{d2}}{K_{sw2}^2 r_{d3}} \quad (12)$$

where the numbers in subscript refer to the number of the system under consideration. The ratio of swelling coefficients for resins with 2% and 8% of cross-linking is known to be  $\sim 1.3$  (ref 29, p 104) and the average radii of resin beads used are equal to  $r_{d2} = 1.5 \times 10^{-2}$  cm and  $r_{d3} = 2.5 \times 10^{-3}$  cm, respectively. Finally, from eq 12 one can obtain  $S_3:S_2 = 3.5$ .

B. The  $^{11}B$  NMR analysis of the initial TMAB and of TMAB- $d_3$  obtained in studying system 4 (Figure 10, a and b, respectively) were recorded with a broad-band probe in a 5-mm NMR tube ( $^{11}B$  resonance at 128.4 MHz), using a tip angle of  $90^\circ$  (6  $\mu s$ ), a pulse repetition time 1 s.  $CDCl_3$  was used as a frequency lock. External referencing of  $^{11}B$  spectra was made by taking the signal for boron trifluoride etherate in  $CDCl_3$  at  $\delta = 0.0$  ppm. The  $^{11}B$

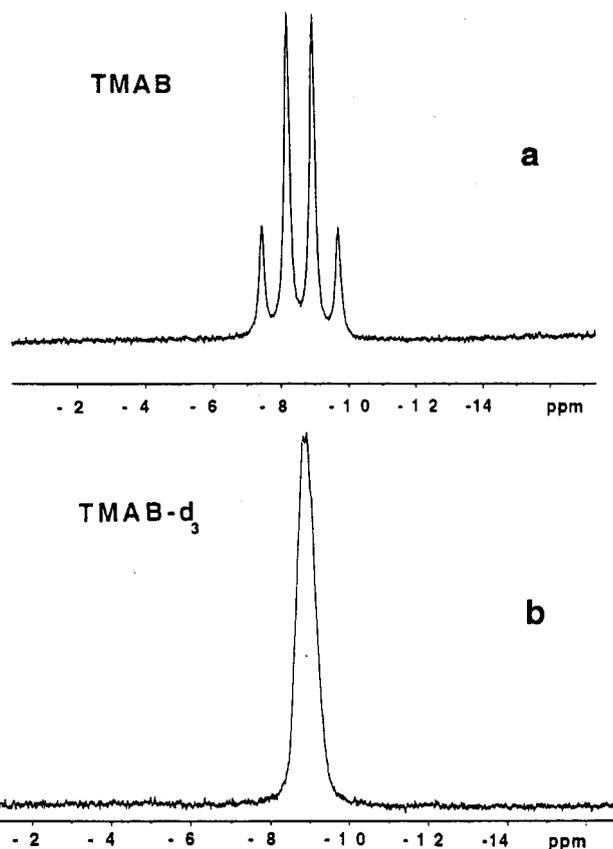


Figure 10.  $^{11}B$  NMR spectra of (a) TMAB and of (b) TMAB- $d_3$  obtained 500 min after starting the kinetic experiment shown in Figure 6 (system 4).

NMR spectra shown in Figure 10 confirm the formation of spectroscopically pure TMAB- $d_3$  obtained in studying system 4.

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