Organic Process Research & Development **1999**, *3*, 352−356

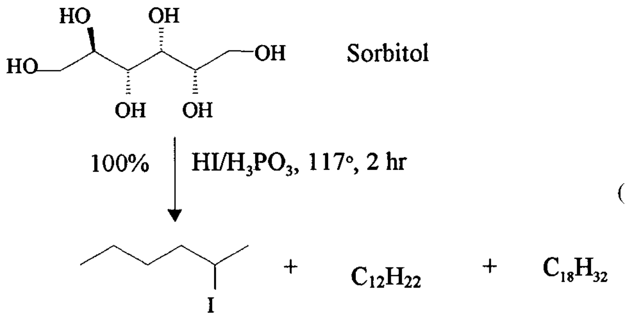
Regeneration and Recovery of Hydriodic Acid after Reduction of Polyols to Fuels[1]

J. Michael Robinson,* Paul T. Herndon, Preston L. Holland, and Laura D. Marrufo

Discipline of Chemistry, Department of Science and Mathematics, The University of Texas of the Permian Basin, Odessa, Texas 79762, U.S.A.

Abstract:

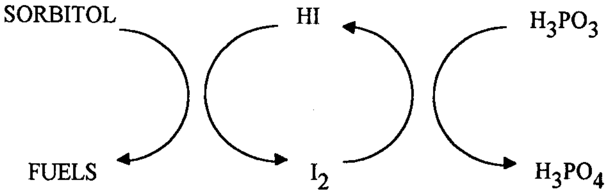
Polyols such as sorbitol, now directly available from biomass carbohydrates, are reduced by hydriodic acid (HI) to hydrocarbon fuels (80%) with some alkyl halide (20%) according to a new process (eq 1). Incipient iodine (I_2) is reduced and returned to hydriodic acid (HI) in situ by the simultaneous use of either phosphorous acid (H_3PO_3) or hypophosphorous acid (H_3PO_2) rather than elemental red phosphorus. The acid mixture can be reused many times. Eventually, HI must be recovered from the ever-increasing amount of phosphoric acid and water in the mixture. The recovery process consists of two to three distillation steps but for safety reasons combines an initial air oxidation of any excess H_3PO_3 to H_3PO_4. ^{31}P NMR conveniently monitors phosphorus moieties. Less than a mmol/L of HI remains in the final phosphoric acid pot residue. This coupled redox combination of reducing acids may allow other industrial uses of otherwise expensive HI at the lesser expense of H_3PO_3 or H_3PO_2, either of which also provide the benefit of a homogeneous system.



(1)

Polyols such as sorbitol, now directly available from biomass carbohydrates such as cellulose or starch, are reduced by hydriodic acid (HI) to hydrocarbon fuels (80%) with some alkyl halide (20%) according to a new process as illustrated in eq 1.[2] The reaction is highly tunable. To gain more hydrocarbons versus halocarbons as shown, the percent of water is adjusted from 35 up to about 48%. However, the reaction does not proceed if too much water is added and the temperature of reflux falls below 115 °C at ambient pressure. The nature and use of these mixtures of branched cyclic and bicyclic hydrocarbons or of subsequent conversions of iodoalkanes to alkenes, alkanes, alcohols, ethers, etc. are the subject of other papers presented and in progress.[2] The focus in this paper is on the economic utility and the safety concerns involved in recycling the expensive HI reagent.

Scheme 1. **Coupled Reduction (in situ)**



Incipient I_2, formed during the reduction of polyols with HI, is immediately reacted and recycled in situ with the completely dissolved phosphorous acid (H_3PO_3) or hypophosphorous acid (H_3PO_2) to regenerate HI as shown in the coupled reduction reactions of Scheme 1. Hypophosphorous acid (H_3PO_2) reacts rapidly with I_2 in HI at room temperature.[3] In fact, H_3PO_2 is used commercially in small amounts to preclude concentrated HI reagent from containing small amounts of I_2 from incidental air oxidation.[4] Phosphorous acid (H_3PO_3) reacts only very slowly with I_2 at ambient temperature but is indeed rapid at the boiling point of the solution.

As droplets of products are produced in this reaction, they coalesce to form an immiscible organic layer (fuels) which

---

(1) Presented in part at the 212th American Chemical Society National Meeting, Orlando, FL, August 26−September 3, 1996, INOR Abstract No. 139.

(2) (a) Robinson, J. M. Process for Producing Hydrocarbon Fuels. U.S. Patent 5,516,960, May 14, 1996. (b) Robinson, J. M.; Banuelos, E. B.; Barber, W. C.; Burgess, C. E.; Chau, C.; Chesser, A. A.; Garrett, M. H.; Goodwin, C. H.; Holland, P. L.; Horne, B. O.; Marrufo, L. D.; Mechalke, E. J.; Rashidi, J. R.; Reynolds, B. D.; Rogers, T. E.; Sanchez, E. H.; Villarreal, J. S. Chemical Conversion of Biomass Polysaccharides to Liquid Hydrocarbon Fuels and Chemicals. ACS FUEL Chemistry Preprints **1999**, *44(2)*, 224. (c) Reduction of Gluconic Acid with Hydriodic Acid to Form Caprolactones. Robinson, J. M.; Chesser, A. A.; Marrufo, L. D.; Villareal, J. S.; Goodwin, C. H. 215th American Chemical Society National Meeting, Dallas, TX, March 29−April 2, 1998, ORGN Abstract No. 192. (d) High Boiling Alcohols and Ethers for Fuel Blending from Renewable Biomass Resources. Robinson, J. M.; Brasher, C. D.; Mandal, H. D.; Marrufo, L. D.; Mouton, S. L.; Ornales, F.; Williams, K. O. 212th American Chemical Society National Meeting, Orlando, FL, August 26−30, 1996, ORGN Abstract No. 336. (e) Chemical Reduction of Biomass Polysaccharides to Liquid Hydrocarbon Fuels. Robinson, J. M.; Alaniz, N. J.; Beech, D. J.; Brasher, C. D.; Burgess, C. E.; Chau, C.; Fields, R.; Herndon, P. T.; Holland, P. L.; Mandal, H. D.; Marrufo, L. D.; McCleery, R. B.; Miller, J. L.; Mills, S. C.; Mouton, S. L.; O'Hara, K.; Ornales, F.; Reynolds, B. D.; Williams, K. O.; Valentine, R. W. 212th American Chemical Society National Meeting, Orlando, FL, August 26−30, 1996, ORGN Abstract No. 148. (f) Robinson, J. M. A Mild, Chemical Conversion of Cellulose to Hexene and Other Liquid Hydrocarbon Fuels and Additives. ACS Fuel Chemistry Preprints **1995**, *40*(3), 729.

(3) Griffith, R. O.; McKeown, A.; Taylor, R. P. *Trans. Faraday Soc.* **1940**, *36*, 752.

(4) (a) Foster, L. S.; Nahas, H. G., Jr. Hydriodic Acid: Regeneration of Oxidized Solutions. *Inorg. Synth.* Vol II, 210, Fernelius, W. C., Ed., **1946**, (b) Heisig, G. B.; Frykholm, O. C. Hydriodic Acid, Procedure A: *Inorg. Synth.* **1939**, *1*, 157. Caley, E. R.; Burford, M. G. Procedure B: *Inorg. Synth.* **1939**, *1*, 159.

10.1021/op990181t CCC: $18.00

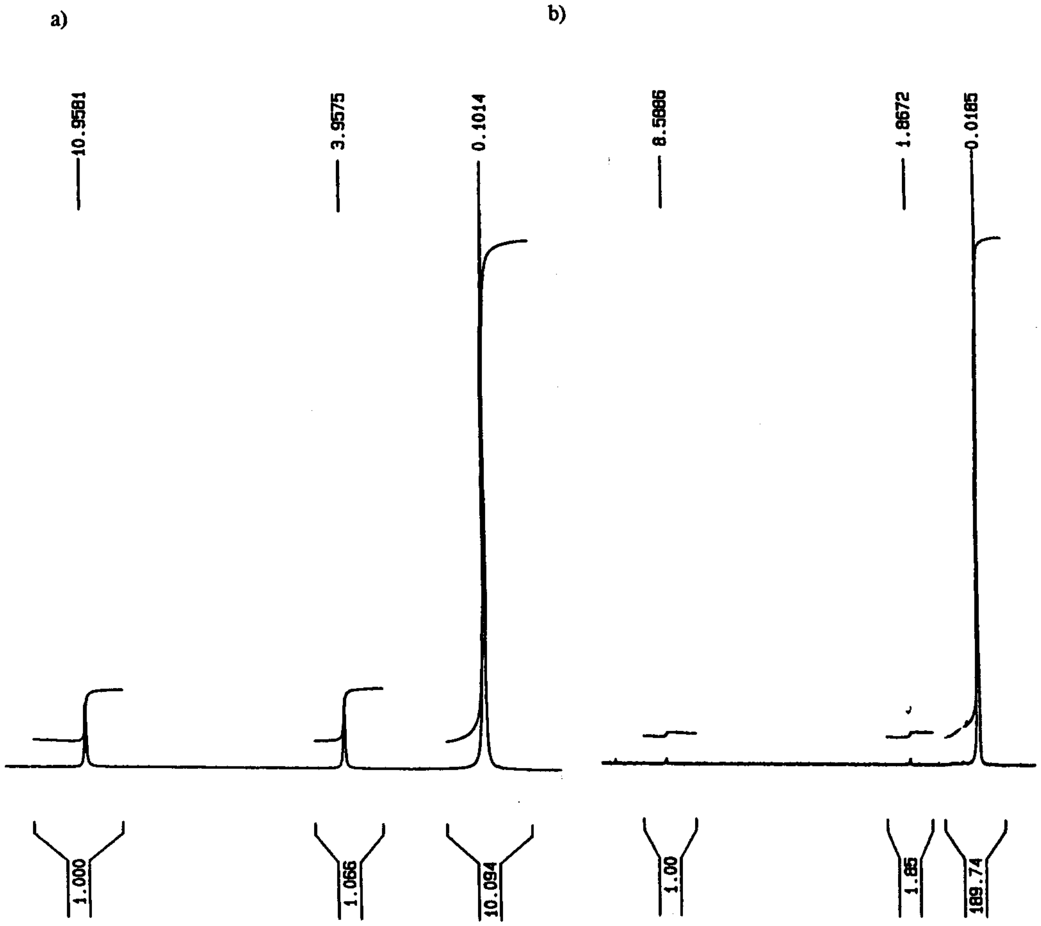


Figure 1. **Phosphorous NMR spectra.**

eventually is simply phase-separated from the otherwise completely homogeneous aqueous mixture of HI/H_3PO_4 acids. This acid mixture of HI/H_3PO_4 can be reused several times before regeneration is required. Subsequent reactions are thus conducted by adding polyol and H_3PO_3 to the HI/H_3PO_4 mixture. For example, 3−5 batches, each of about 0.8 mol of polyol and a proportionate amount of H_3PO_3 were added to one reaction flask before the acid mixture was recycled. Eventually, the hydriodic acid has to be recovered from the ever-increasing amounts of phosphoric acid in the mixture. The gradual dilution of HI with H_3PO_4 apparently does not effect this reduction system in the ranges investigated. In our process, the preferred mole ratio of reagents is about 1:9:5 of sorbitol to HI to H_3PO_3. After two or three subsequent additions of reactants, there is about a 9:10 or 9:15 ratio, respectively, of HI to H_3PO_4 byproduct. However, any dilution with water does change the reflux temperature of the aqueous phase. Flask size provides perhaps a reasonable limit to the reuse of this acid mixture before regeneration, at least for lab scale reactions.

The recovery of HI primarily in the form of concentrated acid for reuse is accomplished in two to three distillation steps. For SAFETY reasons, the last traces of remaining phosphorous acid must be destroyed either before distillation or during the first stage of distillation. This avoids a thermally induced decomposition of H_3PO_3, presumably resulting in pyrophoric white phosphorus as the distillation pot temperature rises during the final stage of distillation. For example, a distillation was conducted on a batch of acids in which the destruction of the phosphorus reagent had not been conducted. At the end of the distillation of concentrated HI when the flask was opened to air, there were locally minute pyrophoric decompositions of the phosphorus that resembled “sparklers” inside the distillation flask. This occurred at many points all over the liquid surface. Small residues of fuel or wax that remained in the flask were then ignited (FIRE!) and continued burning until exhausted (several minutes).

To preclude this fire hazard, destruction of all but traces of unreacted H_3PO_3 is required. Large excesses of phosphorus reagent(s) can first be reacted with more substrate. Facile oxidation of remaining traces of H_3PO_3 is accomplished with a stream of air introduced into the boiling solution during the initial fractional distillation to remove excess water from the system. ^{31}P NMR easily monitors phosphorus moieties before and during the air oxidation reaction. A sample of the concentrated acid solution is placed directly in a 5-mm NMR sample tube. Spectral data is collected in the completely coupled mode. Thus, the characteristic doublet (J_{PH} = 700 Hz) provides conformation of H_3PO_3 and is less likely to be confused with a singlet for the internal standard H_3PO_4. Figure 1a shows an example of a sizable amount of remaining H_3PO_3 ($\delta \sim 6.5$, d, $J_{HP} \cong 700$ Hz)[5] and no H_3PO_2

---

(5) Gallagher, M. J. ^{31}P NMR Data of Four Coordinate Phosphorous Compounds Containing A P═Ch Bond and One or Two P−H Bonds. In CRC Handbook of Phosphorous-31 Nuclear Magnetic Resonance Data; Tebby, J. C., Ed.; CRC Press: Boca Raton, FL, 1991; Chapter 10, pp 287−296.

Table 1. **Primary HI Recovery**

fraction	vol (%)	HI recov. (%)	comments
1. forerun (dil. acid)	0−10	(≤1)	easily recycled
2. concd acid (55−57%)	40−50	98−99	need concd acid for reactions
3. pot residue (H_3PO_4)	∼50	∼1	must recover if large scale

(δ 3.8/12.7, t, $J_{HP} = 565$ Hz) in the HI/H_3PO_4 solution before destruction with air. Figure 1b shows only traces of H_3PO_3 remaining after this air driven oxidation at distillation temperatures. Excessive oxidation to darker iodine solutions should not be allowed either; distillation of such will result in iodine crystals forming in and potentially plugging the condenser.

Table 1 shows typical recovered amounts of HI from our reactions, but these amounts depend on the ratios of reagents used and the type and amount of substrate reacted. The first distillation requires a fractional distillation procedure to remove excess water up to the point where a constant boiling azeotrope of concentrated HI can then be distilled. A small variable amount of HI is collected, but this dilute acid forerun can be easily used in the next reaction.

After excess water is fractionally removed, concentrated HI is then easily distilled. The vast majority of HI (98−99%) is thus recovered and reconstituted to afford full strength acid in this fraction. At the end of the distillation of concentrated HI, the pot residue contains mainly concentrated H_3PO_4 along with a small amount of HI (∼1%). Such a small amount of HI, like the forerun, is not important on a laboratory scale but should not be wasted if used on a large industrial scale. Not only might this add some further cost to the product produced by this process, but it might also adversely affect supply costs (natural resource limits) over a period of several years. For example, in our case, if a small amount of iodine were wasted with each recycle, the world supply of iodine reserves might be exhausted in just a few years of making very large volumes of liquid fuels from biomass.[6]

Therefore, it is appropriate to consider "secondary" HI recovery for potential large scale industrial uses. One method is to add deionized water (batch) to the "primary" recovery pot residue (crude H_3PO_4) and redistill using simple distillation. When such a distillation was conducted (Procedure A) and the distillate analyzed, the results demonstrated a 99% recovery of the *remaining* HI. Final losses due to HI remaining in the phosphoric acid are reduced by more than 50-fold or to less than a mmol/L, which in our case equates to less than two cents per gallon of hydrocarbon fuel ($0.02/gal) makeup cost for HI.[7] Absolute recovery of this resource may need to be achieved if such a process is utilized on a large scale.[8]

The major disadvantage to this batch method of secondary HI recovery is that a substantial amount of water is distilled. Alternatively, if water is added dropwise to the pot and HI is continuously distilled, then comparable results to the batch addition is obtained but surprisingly with an even greater volume of water. Furthermore, the more linear rate of HI recovery with such dropwise addition of water is less desirous. The apparent lag in recovery of HI in a more concentrated form suggests that a reaction/equilibration time is needed so that some phosphorus−iodide moiety (acid halide?) is decomposed to liberate free HI after the addition of water and before this solution is again distilled. Perhaps even a small amount of water (50 mL?) would then be sufficient to recover the last traces of HI. A third method (procedure C) would be to continue distillation of the primary HI recovery pot residue but now under vacuum to a higher pot temperature. These conditions allow further dehydration of the H_3PO_4 solution (presumably from 85 to 100%) at 150 °C and can be continued even further to give pyrophosphoric acid at 200 °C. Procedure C may be the most advantageous since it provides an internally generated water sweep for the continued azeotropic distillation of HI. Disadvantages of Procedure C are that higher pot temperatures are required and less well-defined phosphoric acid−pyrophosphoric acid mixtures result. However, water may be added to the final pot mixture to adjust the phosphorus content as might be required for marketing. Again, care must be taken to ensure that no excess phosphorous acid is present or dangerous decompositions will occur at these higher pot temperatures.

Use of expensive HI[9] as a reducing agent thus becomes more attractive since it can now be safely recycled and reconstituted to full strength acid. The expense of the "reducing agent" for these HI reactions is actually that of the directly coupled and consumed phosphorus reagents, H_3PO_3 or H_3PO_2,[10] rather than the cost of HI. These costs range from 17 to 2% of the cost of HI. Distillation costs would of course add to the total cost of the process. If the byproduct phosphoric acid(s) can be sold,[11] then this revenue can further lower the costs of any reduction application using this HI/phosphorous acid(s) system. Furthermore, use of this HI/H_3PO_3 (or H_3PO_2) reducing acid mixture furnishes a totally homogeneous solution. Previous use of HI for a variety of similar reductions have been accomplished by the simulta-

---

(6) Dan Tyndall of the National Renewable Energy Laboratory (NREL), Golden, CO, provided resource information.

(7) This "make up" cost will be considerably lower the more the HI is reused in reactions before this distillation−reconstitution method is conducted.

(8) Air oxidation of traces of HI to I_2 followed by sublimation may prove acceptable.

(9) Bulk prices for HI (57%) were quoted by Deepwater Iodides, Woodward, OK, at $4.06/mole (1999).

(10) (a) Bulk prices for H_3PO_3 (solid) and H_3PO_2 (50% in H_2O) were $0.16/mole and $0.31/mole, respectively, from Phosphinic (Hypophosphorous) Acid, $H(H_2PO_2)$ or H_3PO_2. *Kirk Othmer Encyclopedia of Chemical Technology*, 3rd. ed.; 1978; Vol. 17, pp 520−23. These prices may be $0.55/mole and $1.06/mole for high purity reagents today (Rhône-Poulenc). (b) A private communication with Oxychem in 1997 remarked that "impure byproduct H_3PO_3" may be available at ∼$0.40/lb (∼$0.07/mole) from alkyl halide and carboxylic acid chloride processes.

(11) Bulk price for technical grade 85% H_3PO_4 is $0.097/mole. Current quote from FMC and Monsanto.

neous use of solid red phosphorus.[12] The resulting heterogeneous mixtures were difficult to stir and very slow to react, the products were difficult to purify, and unreacted moieties presented difficult disposals. More importantly, however, is the fact that perhaps even different reduction products might be available with the use of our fast reacting homogeneous HI/H_3PO_3 (or H_3PO_2) system.[2]

Experimental Section

Production of C_6, C_{12}, C_{18} Products from Sorbitol (Example of Sequential Batch Method). Using a three-neck (ST 24/40), 3-L flask with two Freidrich's condensers, D-sorbitol (150.1 g, 98%, 0.8 mol), hydriodic acid (HI, 980 mL, 57%, 7.2 mol), phosphorous acid (H_3PO_3, 372.3 g, 97%, 4.4 mol), and deionized water (200 mL) were refluxed (118 °C) under a nitrogen atmosphere for 2.5 h. **CAUTION:** The reaction becomes quite exothermic at about 100 °C and will often exceed the cooling capacity of one condenser for this scale of reaction. The solution was allowed to cool for 20 min. D-Sorbitol (150.1 g, 98%, 0.8 mol), H_3PO_3 (338.5 g, 97%, 4.0 mol), and H_2O (260 mL) were then added, and the solution was refluxed overnight. The product (top layer) was then separated from the aqueous acid (bottom) by means of a separatory funnel. The total product was 149.8 g. GC/MS analysis allowed an estimation of the amount of products: $C_6I = 6.6\%$; $C_{12} = 42.7\%$; $C_{18} = 46.1\%$, and $C_{24} = 5.4\%$. The additional water added to the reaction, in this case to gain more hydrocarbons, limits the reaction to about 2.4 mol of sorbitol per 3-L flask. This experiment used only 1.6 mol. This method allows for the instantaneous ratio of HI to be high (1:9) but finally results in a 1:4.5, or 1:3, etc., range of total polyol reacted to total HI used.

Fractional Distillation of Dilute HI to Remove Excess Water. A triple neck, 3-L, round-bottom flask was supplied with an air inlet tube bleed under the liquid surface, fractionating column, and thermometer to measure the temperature of the liquid. A distillation head with a thermometer was connected at the top of the fractionating column, then to two condensers followed by a vacuum relief and dry ice/acetone vapor trap. An impure dilute HI mixture resulting from biomass to fuel reactions (2.000 L) was distilled at ambient pressure until either the head temperature was ~125 °C or until the pot temperature was ~140 °C. The volume collected in this experiment was 186 mL (9.3 vol %). This volume will vary, depending on the dilution of the waste HI to be redistilled. The majority of the distillate was water, but some HI was purposely distilled to get the head temperature up to 125 °C for subsequent recovery of highly concentrated HI. The temperature rises quickly during the last few mL of distillate.

^{31}P NMR. Samples (1 mL) of the acid mixture are placed directly into a 5-mm tube and either 8 or 16 transients are collected with a Bruker Avance 250 instrument. The H_3PO_4 byproduct serves conveniently as the internal standard (^{31}P ν =101.254 MHz). Because of the variety of concentration effects of this HI system, the actual chemical shift of H_3PO_3 contained therein varied from δ 5.24−8.52 with J = 673−714 Hz. The literature reports a range of δ 1.7−8.0 with J = 694−700 Hz.[5] Addition of D_2O for a lock solvent was not necessary for this analysis.

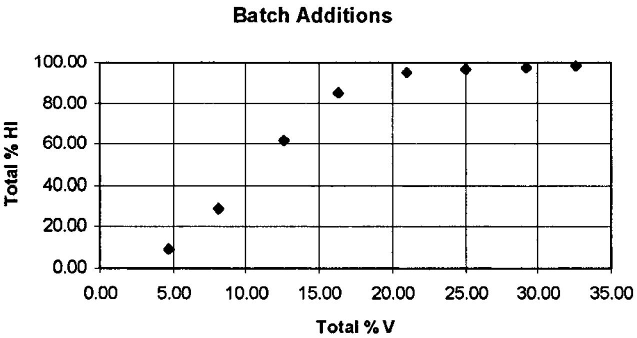


Figure 2.

Table 2. **Secondary HI Recovery (Batch Additions Procedure A)**

additions (mL)	distillation cuts (mL)	HI (%)	V (%)	cumulative total V (%)	cumulative total HI (%)
250					
	67	9.37	4.66	4.66	9.37
	50	19.80	3.47	8.13	29.18
	64	32.36	4.45	12.58	61.53
	54	23.54	3.75	16.33	85.07
	67	9.89	4.66	20.99	94.96
50					
	58	1.67	4.03	25.02	96.64
50					
	61	1.21	4.24	29.26	97.85
50					
	48	0.89	3.34	32.59	98.74
final pot	970	1.26	67.41	100.00	100.00
total	1439	100	100		

Table 3. **Continuous Drip Additions (Procedure B, 455 mL)**

additions (mL)	distillation cuts (mL)	HI (%)	V (%)	cumulative total V (%)	cumulative total HI (%)
72	50	11.74	3.38	3.38	11.74
69	50	8.63	3.38	6.77	20.37
48	50	8.35	3.38	10.15	28.72
37	50	8.42	3.38	13.53	37.15
39	50	9.27	3.38	16.91	46.41
43	55	10.04	3.72	20.64	56.45
36	50	9.69	3.38	24.02	66.15
38	50	9.97	3.38	27.40	76.12
38	50	10.61	3.38	30.78	86.73
35	50	12.76	3.38	34.17	99.49
final pot	973	0.51	65.83	100.00	100.00
total	1478	100.00	100.00		

Vacuum Distillation of Concentrated HI. The process is then switched to a simple (not fractional) distillation under vacuum. If there is no remaining H_3PO_3 to oxidize (as determined by ^{31}P NMR), the air bleed is also removed from the distillation pot. Concentrated hydriodic acid (~57%) azeotrope is then distilled, collecting in this example, 744 mL plus 30 mL from the cold trap (774 mL, 5.9 mol) within a 77−82 °C boiling range (~155 mmHg). The pot temperature rose to 140 °C (~155 mmHg). Analysis of the pot

---

(12) Vincent, C.; Delachanal Work with Sorbitol. *Compt. Rend.* **1890**, *109*, 677 (French); *Beil.* **1918**, First Work, Band I, System 59, 533.

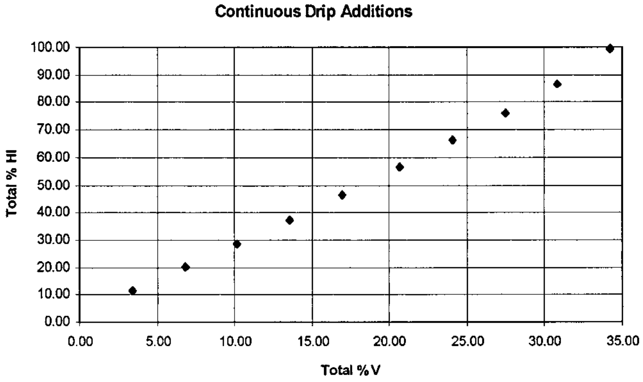


Figure 3.

residue of H_3PO_4 (1039 mL) showed that it contained 57.52 mmol of HI.

Recovery of Small Amounts of HI from H_3PO_4. Procedure A: Sequential Batch Addition of H_2O and Continuous Distillation. Water (250 mL) was added and again distilled with vacuum while fractions were taken. Small subsequent batches proved to be less efficient; see Table 2 and Figure 2 for details.

Procedure B: Dropwise Addition of Water with Constant Distillation. See Table 3 and Figure 3 for the comparable, albeit less desired, dropwise addition of water. The rate of addition of water was slightly greater than the rate of distillation.

Procedure C: Continued Distillation of HI from 85% H_3PO_4. This method, while not performed separately, was suggested by the fact that 69 mL and 50 mL of excess water was removed from the distillations in procedures A and B, respectively, than was actually added. No attempt was made to optimize this procedure. **CAUTION:** All reducing phosphorus moieties must be absent to SAFELY go to these higher pot temperatures of procedure C.

Acknowledgment

A Chemistry Department Grant from the Robert A. Welch Foundation (Texas) and a grant from the U. S. Department of Energy, Basic Energy Sciences, Advanced Research Projects have supported this research.

Received for review December 16, 1998.

OP990181T