LETTERS TO THE EDITOR

Loss of HBr in Toluene Solutions: a Kinetic Study

Sir: In his comparison of the several methods proposed for determing cyclopropenoid fatty acid esters in vegetable oils, Coleman (J. Ass. Off. Anal. Chem. 53:1209[1970]) observed a continuous loss in strength of the HBr reagent used in the method proposed by Feuge and coworkers (JAOCS 46:185[1969]). We are in agreement with Coleman that there is a continuous loss in strength of the HBr reagent as it is prepared and stored in accordance with Feuge. Data are shown in Table I. Here the initial datum was obtained 1 hr after the stock solution was prepared. The data in column 2, namely $(a - x)$, are concentrations of HBr at the respective times.

The HBr reagent (maintained at room temperature in the Machlett buret) was completely closed to the atmosphere all the time, with the exception of the admission of dry air into the chamber to permit delivery of metered quantities of HBr solution into the titration chamber.

Evidently the relationship

$$k = \frac{1}{t_2 - t_1} \log \frac{a - x_1}{a - x_2}$$

is derived from the first order rate equation

$$kt = \log \frac{a}{a - x}$$

where a is the initial concentration of HBr and x_1 is the quantity, expressed as equivalents per liter, lost in the time t_1.

A regression analysis of the data in Table I, using the 21 combinations constructed from the data, yielded a regression coefficient of 0.0231 for the regression on $(t_2 - t_1)$ and the reciprocal of a regression coefficient of 0.0233 for the regression on $\log (a - x_1)/(a - x_2)$, and a correlation coefficient between $(t_2 - t_1)$ and $\log \frac{a - x_1}{a - x_2}$ of 0.99. Obviously the data conform to the rate equation for the first order reaction.

We refer again to the rate equation and write

$$kt_1 = \log \frac{a}{a - x_1} \quad \text{and}$$

$$kt_2 = \log \frac{a}{a - x_2}$$

TABLE I

Decrease in Strength of HBr Solution with Time

Age of solution, hr	Average (of duplicate analysis) of HBr solution, N
1	0.0478
2	0.0464
3	0.0456
4	0.0438
5	0.0414
20	0.0298
23	0.0279

When $t_2 = nt_1$, one may divide the one equation with the other, and on rearrangement it is readily seen that

$$a^{n-1} = \frac{(a - x_1)^n}{a - x_n}$$

Thus it is possible to estimate the initial concentration of HBr from the data in Table I. The results are shown in Table II. The mean value for the initial concentration of HBr is estimated to be 0.0486 ± 0.002 N, at the 5% level of probability.

The constancy of the estimated initial concentration of HBr, as obtained from the data in Table I, also indicates that the data in Table I conform to the first order rate equation.

It was observed that the toluene solution turned red with time, and small droplets of a red liquid separated as a second phase. A red color developed much more slowly when the reagent was stored in the dark. It is known that gaseous HBr is decomposed photochemically (Tingey and Gerk, J. Amer. Chem. Soc. 48:1838[1926]). Evidently HBr in toluene solution is also decomposed by light. (The photochemical decomposition of HBr is notorious; this is the reason it is not used generally as a reagent in acidimetry. The chemistry involved here in this report is $2HBr + H_2 + Br_2$; $Br_2 + C_7H_8 \rightarrow C_7H_7Br + HBr$. The evidence, in addition to the kinetic data, is as follows: Dry HBr was passed into dry toluene and the solution was permitted to stand in the laboratory for ca. 1 month. The solution was then concentrated. The UV spectrum, with toluene serving as the reference, showed a strong adsorption in the region of 280-340 μ. The concentrate was then treated with nitric acid and a yellow crystalline material was separated. This was subjected to fusion with sodium and the filtrate recovered from the fusion treatment was acidified slightly with nitric acid, boiled to expell any HCN that might have formed, and then added to a dilute solution of silver nitrate. A white precipitate formed that turned dark on standing in the light. HBr was the source of the halogen found in the crystalline material.)

EXPERIMENTAL PROCEDURES

Preparation of HBr Solution in Toluene

The HBr reagent (HBr in dry toluene) was prepared as

TABLE II

Estimation of Initial Concentration of HBr

Time, hr		Estimated concentration of HBr, N
Initial	Final	
1	2	0.0492
2	4	0.0492
1	3	0.0489
1	4	0.0493
1	5	0.0495
5	20	0.0462
4	20	0.0483

directed by Feuge et al. and stored in the chamber of a Machlett automatic buret.

HBr reagent was also prepared from HBr generated from a saturated aqueous solution of KBr on the addition of concentrated sulfuric acid. The HBr generated by the reaction was dried by passing it through concentrated sulfuric acid, and the bromine vapors, resulting from the oxidation of HBr by sulfuric acid, were condensed before the gas stream was passed into dry toluene. Qualitative tests for Br_2 in the toluene solution were negative. This solution was also stored in the chamber of a Machlett automatic buret. Continuous loss of HBr was observed with each preparation we studied.

In each case the automatic buret was equipped with a three-way Teflon stopcock, and the delivery tip was modified to receive a no. 18 gauge hypodermic needle.

Titration of HBr

A Teflon-coated magnetic bar and two drops of phenolphthalein indicator were placed in a 250 ml narrow neck bottle, and the bottle was warmed on a water bath at 50-55 C and immediately stoppered with a serum bottle stopper with a retractable sleeve. The bottle was then cooled to room temperature to reduce the pressure inside to facilitate subsequent operations.

The hypodermic needle attached to the automatic buret was plunged through the serum stopper, and a metered quantity of HBr solution was delivered into the bottle and the needle withdrawn. The bottle was then placed above a rotating magnetic bar, and standard KOH (0.1077 N in ethyl alcohol) was delivered into the bottle through a hypodermic needle by means of a mechanically driven and calibrated infusion pump (Aminco No. 4-2340, Patent 2,925,198) until a faint pink color developed and remained permanent. The delivery of the KOH solution (either continuous or intermittent) was positive.

Very careful observations revealed no loss of HBr to the atmosphere under the conditions used. No stopper was reused for a second titration, and in no instance did the hypodermic needle serve as an opening to the atmosphere.

VERNON L. FRAMPTON
W.J. EVANS
J.C. KUCK
Southern Regional Research Laboratory
ARS, USDA
New Orleans, Louisiana 70179

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Preparation of Methyl Esters of Long Chain Fatty Acids

Sir: For some time we have been successful in using $HClO_4$ in place of boron trifluoride for transesterification of triglycerides of fatty acids to form corresponding methyl esters. This has several advantages. Perchloric acid is commercially more available and less expensive than boron trifluoride, and under the following reaction conditions perchloric acid is not hazardous. The transmethylation technique is (AOCS Method Ce 2-66): Introduce 0.5 g oil or fat into 50 ml round bottom reaction flask. Add 0.8 ml 0.5 N methanolic NaOH. Attach condenser and reflux on steam bath until fat globules dissolve (10 min). Add 0.8 ml 60% $HClO_4$ through condenser and continue refluxing for 2-3 min. Add 5 ml heptane and boil 1 min. Remove from head and add enough saturated NaCl solution to float heptane solution of methyl esters into neck of flask. Transfer as much heptane solution as possible into dry test tube. Add small amount of anhydrous Na_2SO_4. Dry heptane solution is ready to be injected directly into gas chromatograph.

P.J. MAVRIKOS
G. ELIOPOULOS
State General Chemical Laboratories
Research Section
16 A. Tsoha St.
Athens, Greece

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