uring the viscosity of a 3.6% sucrose solution at 25°, taking the figures given by Gosting and Morris[5] as standard. Kinetic energy corrections were found to be negligible.

The junior author is indebted to the University of Western Australia for a Hackett Scholarship during the tenure of which this work was done.

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[5] L. J. Gosting and M. W. Morris, This Journal, 71, 1998 (1949).

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Purification of Tetraethylenepentamine

By E. H. Gause, T. B. Crumpler and H. B. Jonassen

Tetraethylenepentamine, $NH_2C_2H_4NHC_2H_4NHC_2H_4NHC_2H_4NH_2$, has recently become of importance as a colorimetric reagent[1] and as an activator in low temperature copolymerization.[2] However, in both these instances relatively impure pentamine was used. The peculiar form of the graph obtained by Crumpler[1] depicting the effect of excess pentamine on color development with Cu^{++} ion suggested the need for a study of the complexes existing in solution. The purified sample is being used for a continuous variations study. Spolsky and Williams[3] noted the presence of iron in their pentamine samples and suggested the desirability of a study to differentiate the functions of iron and pentamine in the activator effect.

Previous attempts in this Laboratory to isolate this amine by fractional distillation and by the selective precipitation of normal as well as acid salts of various anions were unsuccessful. We have now succeeded by an ion exchange method in separating pure pentamine from the commercially available material which contains lower and higher molecular weight polyamines as well as an appreciable amount of iron.

Further work is in progress to determine the structure and stabilities of the complexes formed between the various metal ions and pentamine similar to that with the lower amines.[4]

Experimental

An ion exchange column 90 cm. in length and 2.2 cm. in diameter, containing the acid form of 250–500 mesh Ion-X (Dowex-50) resin was prepared. A thick slurry of the resin in distilled water was poured into the column which was partially filled with water and the resin bed was allowed to settle. A liter of solution of commercial tetraethylenepentamine (40 g./l.) was decolorized with Norit and passed through the column under about 300 mm. pressure. The amines were absorbed on approximately $^1/_3$ of the column. The column was then washed with distilled water and eluted with 0.25 *N* NaOH. The flow-rate was 0.7 cc./min. The passage of the amine layer down the column can be followed readily because of the difference in color of the several forms of the resin. The amine solution was collected in 50-cc. fractions. The eluted amine was slightly discolored; therefore, alternate fractions were decolorized with 0.5 g. of Norit and a 25-ml. aliquot diluted with 100 cc. of water, saturated with HNO_3, and titrated potentiometrically with 0.5 *N* HNO_3. Standard HCl and KCl, supporting electrolyte, may also be used. Fractions 5, 7, 9 and 11 were mainly tetraethylenepentamine together with some impurities.

The combined pentamine fractions, together with their even-numbered counterparts (250 cc.) were treated with Norit. They were then passed through a column (29 × 1.7 cm.) operated by an aspirator, at a flow-rate of 0.9 cc./min. and eluted with 0.25 *N* NaOH as described above. Again 50-cc. fractions were collected and 10-ml. aliquots titrated with 0.2 *N* HNO_3 with KNO_3 as supporting electrolyte. The following yield was obtained. (1) Fractions 1 and 2 were pure pentamine solution; (2) fraction 3 was 95% pure pentamine solution; and (3) fraction 4 was a highly impure mixture.

In order to eliminate discoloration which was probably the result of decomposition encountered using the acid form of the resin, attempts were made to adsorb the amine on both the sodium and potassium resins, but in the concentrations used in this work, the aminium ions would not replace the alkali metal ions.

It is important that the resin bed be kept in contact with liquid at all times. If allowed to run dry, channeling will occur, permitting mixing of the NaOH and amine solutions. Should this occur, the Na^+ ions may be removed by passing the solution over a small resin bed, the amount of resin depending on the amount of Na^+ present.

The iron normally present in the commercial tetraethylenepentamine is also removed during the purification. In basic solution the iron–amine complex is strongly adsorbed on the resin, and on reconversion of the resin, is displaced by the acid. Below a *p*H of about 3, the complex is red, and above this *p*H it is yellow. Both basic and acidic solutions of the complex were tested for Fe with $K_4[Fe(CN)_6]$. The acid solution gave a positive test indicating greater stability of the basic yellow form. Some of the complex was oxidized to Fe^{+++} and gave a positive test with KCNS. The eluted amine solution was found to be free of iron by these tests.

The purity of each sample was determined from the titration. The simple titration graph is not satisfactory since only the final inflection point is sharp enough to be accurately located on the curve. The differential plot ($\Delta p\text{H}/\Delta V$ *vs.* V) shows that there are breaks corresponding to the neutralization of the fourth and fifth nitrogen atoms of the molecule with indications of breaks for the second and third. The coincidence in the position of the maxima with their theoretical location is taken as the indication of purity (see Fig. 1).

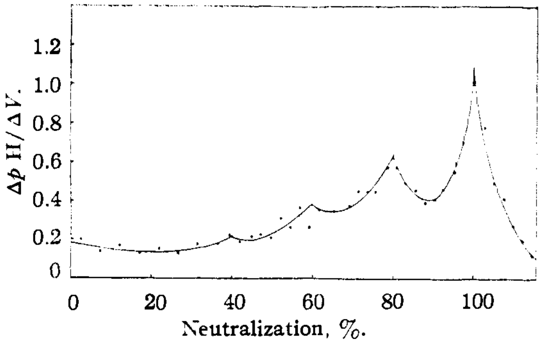

Fig. 1.

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[1] T. B. Crumpler, *Anal. Chem.*, 19, 325 (1947).

[2] R. Spolsky and H. L. Williams, *Ind. Eng. Chem.*, 42, 1847 (1950).

[3] Private communication, H. L. Williams to H. B. Jonassen.

[4] H. B. Jonassen, R. B. LeBlanc and R. M. Rogan, This Journal, 72, 4968 (1950).

The Fluorination of Aqueous Selenious Acid

By John W. George and S. Young Tyree, Jr.

Selenious acid solutions of varying strengths have been fluorinated in an attempt to determine optimum conditions for conversion to selenic acid.

$$H_2SeO_3 + F_2 + H_2O \longrightarrow H_2SeO_4 + 2HF$$

Experimental

Twenty-five ml. of a standardized solution of selenious acid was pipetted into a 35-cc. platinum crucible. With the fluorine cell operating, the platinum delivery tube was introduced into the solution through a hole in the cover. The solution was maintained at steam-bath temperature. Following fluorination, aliquots were analyzed for unoxidized selenious acid.

Table I shows the results of trials on solutions of 0.393 equivalent of selenious acid per 25 ml.

TABLE I

Equiv. F_2	X-fold excess F_2	Conversion to H_2SeO_4, %
1.2	3	46.6
2.8	7	58.0
3.0	7.5	59.8
4.5	11.5	70.8
7.8	19.8	69.8

During the fluorination the volume of the solution was reduced considerably due to evaporation and to reaction between water and fluorine. In all concentration ranges studied, a maximum conversion limit was approached beyond which further fluorination had no effect.

The progressive addition of water during fluorination, such that the volume of solution was held constant, resulted in virtually complete conversion to selenic acid. In all cases a few tenths of a per cent. of unoxidized selenious acid was detected, as has been reported using hydrogen peroxide as oxidizing agent.[1] The X-fold excess fluorine needed to attain $99^{+}\%$ conversion did not vary significantly with the original concentration of selenious acid.

[1] L. I. Gilbertson and G. B. King, "Inorganic Syntheses," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 137.

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Acetolysis Rates of the *cis*- and *trans*-2-Chloro- and 2-Bromocyclohexyl *p*-Bromobenzenesulfonates

BY ERNEST GRUNWALD[1]

In the previous work on the acetolysis of various substituted cyclohexyl *p*-bromobenzenesulfonates,[2] it was important to know the driving forces due to the nucleophilic participation of the neighboring 2-substituents. To evaluate these driving forces, we compared the observed acetolysis rates k with the rates k_C predicted for a mechanism of the carbonium type. Whenever k significantly exceeded the estimate of k_C, a nucleophilic driving force due to the neighboring group was indicated.

In the case of the monatomic or structurally simple neighboring groups such as halogen or OH, values of k_C were calculated[2] from the extra electrostatic work[3] W needed to generate the C–O dipole M_1 of the partly ionized *p*-bromobenzenesulfoxy group in the transition state against the dipole of the neighboring group. In the case of the complex neighboring groups such as acetoxy and *p*-bromobenzenesulfoxy, *a priori* calculation of the carbonium rates was not readily feasible. It turned out[2] that the *cis*- and *trans*-cyclohexane 1,2-di-*p*-bromobenzenesulfonates reacted at slow and nearly equal rates. The *cis*-2-acetoxycyclohexyl *p*-bromobenzenesulfonate also reacted slowly, but the *trans*-ester was several thousand times faster. This contrasting behavior suggested[2] that the *trans*-2-acetoxy group was furnishing a driving force which the *cis*-group, due to its geometry, could not provide. To estimate this driving force, it was assumed that the carbonium rate k_C for the *trans*-compound was nearly equal to the observed rate for the *cis*-compound. Although this assumption seemed reasonable in view of the reactivities of the cyclohexane 1,2-di-*p*-bromobenzenesulfonates further evidence is desirable.

The *cis*- and *trans*-2-chloro- and 2-bromocyclohexyl *p*-bromobenzenesulfonates are excellent models for further study of these points.[4] The neighboring halo-groups are simple enough to permit *a priori* calculation of the carbonium rates k_C with some certainty even for the *cis*-isomers. Thus, some insight may be gained into the acetolysis mechanism of the *cis*-compounds.

The pertinent first-order acetolysis rate constants at 74.9° are summarized in Table I. The new rate constants[5] corroborate our previous conclusions[2] based on data for the *cis*- and *trans*-2-acetoxy- and 2-bromobenzenesulfoxycyclohexyl compounds. In the case of *trans*-2-chlorocyclohexyl *p*-bromobenzenesulfonate where the previous evidence[2,6] had suggested a mechanism of the carbonium type, the rate agrees with that of the *cis* isomer within a factor of 4 (Table I). On the other hand, the *trans*-2-bromo ester reacts 800 times faster than the *cis*-2-bromo ester. This is again consistent with our previous judgment that the *trans*-2-bromine atom is furnishing a nucleophilic driving force.[2,6] The rates of the *cis*-2-chloro- and *cis*-2-bromocyclohexyl esters are nearly equal, consistent with the nearly equal inductive effects of these two atoms.

Beyond their low rates, little is known about the solvolytic reactions of the 2-halocyclohexyl esters. We have calculated the extra electrostatic work W, assuming a mechanism of the carbonium type, on the same basis as before.[2,3] The results, summarized in Table II, predict values of k_C $^1/_{14}$ of the observed rate for the *cis*-2-chloro ester and $^1/_5$ of the observed rate for the *cis*-2-bromo ester. These factors are large enough to make it appear unlikely that mechanisms of the carbonium type

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[1] Visiting Associate Chemist, Brookhaven National Laboratory, June–September, 1950; Department of Chemistry, Florida State University.

[2] S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

[3] J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506, 513 (1938).

[4] The author is grateful to Dr. R. B. Loftfield of the Massachusetts General Hospital for providing him with pure samples of these compounds.

[5] The rate constants listed in Table I measure the acetolysis of the *p*-bromobenzenesulfonate group, not of the less reactive halogen atoms which may also solvolyze. The solvolysis rates of the halogen atoms may be estimated from the relative reactivities, cyclohexyl *p*-bromobenzenesulfonate:cyclohexyl bromide:cyclohexyl chloride $\approx 1:3 \times 10^{-3}:1 \times 10^{-4}$; and k/k_H for a *cis*- or *trans*-2-*p*-bromobenzenesulfoxy substituent $\approx 7 \times 10^{-5}$ (ref. 2). Thus one would expect reaction rates 1/10,000 of the observed rates if the *cis*-chlorine atom was sovolyzing, and 1/500 of the observed rates if the *cis*-bromine atom was solvolyzing.

[6] S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948).