

system studied, and as shown in Figure 8, the distribution ratio depends upon the concentration of acetate ions. In this study the ionic strength was not maintained constant, for chloride affects the synergism and both nitrate and perchlorate react with tetraphenylarsonium chloride. Although the increase of extraction may be due to the salting out effect, the linear relationship of the log of the distribution ratio with log acetate concentration (with a slope of 1) and the fact that acetate must be present for synergism indicate that one mole of acetate is combining with one mole of gallium. The proton magnetic resonance spectra of the complex is further evidence of the presence of acetate ion. We therefore assume that acetate is directly coordinated to gallium along with TTA. In the presence of excess chloride there is no synergism. When the chloride ion concentration is very small and corresponds only to that contributed by gallium chloride and tetraphenylarsonium chloride, then the acetate ion can effect synergism. It has previously been shown that acetate ion in the compound $\text{Ga}(\text{OAc})_3$ is easily replaced by chloride ion to give $\text{GaCl}_2(\text{OAc})$ (11).

In order to form a complex with tetraphenylarsonium cation, gallium should combine with other anionic species. This also meets the requirements for a six coordinated complex. The presence of bromine in the complex prepared from gallium bromide substantiates the participation of chloride ion in the synergic product in the system studied with gallium chloride. Our results are consistent with the reports

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of Nyholm (12) and Greenwood (13) that many different halide-containing complexes occur when gallium complexes are prepared from gallium halides. It has also been reported (11) that in acetic acid, gallium trichloride forms $\text{GaCl}(\text{OAc})_2$ to the extent of 70% of the total gallium, and the replacement of chloride ion is difficult.

From the experimental results and published data, we are of the opinion that in the aqueous phases at low pH trivalent gallium combines with TTA, acetate, and chloride in the ratio of 1:2:1:1 to form an anionic species $[\text{Ga}(\text{T})_2(\text{OAc})(\text{Cl})]^-$ which combines with one mole of tetraphenylarsonium cation to form a neutral ion association complex which is extractable in organic solvent. At pH 2.4 the extraction of gallium with only TTA is low. The distribution ratio is 0.28 and 22% is extracted. This 22% is in the form of $\text{Ga}(\text{T})_3$ neutral complex. However, in the presence of both TTA and tetraphenylarsonium chloride the distribution ratio is 22.6, which indicates that 96% is extracted. From this it might be assumed that at pH 2.4, 74% of gallium remains in the aqueous phase as $\text{Ga}(\text{T})_2(\text{OAc})(\text{Cl})^-$ form, and 22% remains as the neutral $\text{Ga}(\text{T})_3$ complex. It is further assumed that the 4% remains in some form of cationic species.

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Theoretical Evaluation of Entropy Titration Method for Calorimetric Determination of Equilibrium Constants in Aqueous Solution

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The effect of random errors in the titrant and solution concentrations and in the heat data on the accuracy of the equilibrium constant values obtained from thermometric titration data has been determined. Systems of the type $\text{HA} + \text{B}^- = \text{HB} + \text{A}^-$ where K_R is the equilibrium constant for the reaction as written and K is the equilibrium constant for the reaction $\text{HB} = \text{H}^+ + \text{B}^-$ were investigated. The equilibrium constant for the reaction $\text{HA} = \text{A}^- + \text{H}^+$ is assumed to be known. The accuracy with which K can be determined depends on the magnitude of K_R ; the most accurate log K values being obtained when log K_R is greater than -1 and less than 2 . For log K_R values in this range, the cumulative effect of a 0.4% random error in the experimental heat data and of a 0.1% random error in the solution and titrant concentrations will normally cause an error of less than 0.01 unit in log K . Through the proper choice of titrant, the entropy titration method can be used to accurately determine any pK value less than 15 or greater than -1 for proton dissociation in aqueous solution.

THE TERM "entropy titration" has been used (1, 2) to describe the general method developed for the determination of log K , ΔH° and ΔS° values from thermometric titration data. The method has been applied to many systems. For reactions of the type



where HA is the acid constituent of the titrant having a known pK value, and B^- is the basic species protonated in the solution being titrated, the shape of a thermometric titration curve is determined (for given titrant and solution concentrations) by the value of the equilibrium constant, K_R , for Reaction 1. Reactions having the same K_R value but different ΔH_R° values will produce a family of similarly shaped curves, each characterized by a different ΔH_R° value. Once K_R has been evaluated from the thermometric titration curve, it can be combined with the known equilibrium constant for Reaction 2



to calculate the unknown equilibrium constant for Reaction 3.



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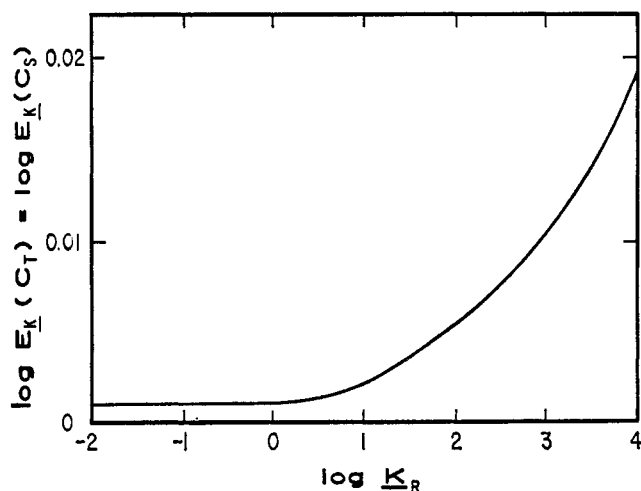


Figure 1. Plot of $\log E_K(C_T) = \log E_K(C_S)$ values vs. $\log K_R$

$|\Delta H_R| \geq 1$ kcal/mole
Error: $\pm 0.1\%$ in C_T or in C_S

In the entropy titration method as developed in this laboratory, experimental Q_R values (corrected for heat of dilution and for nonchemical effects such as the heat of stirring and the thermistor heating) taken from the thermometric titration curve are used to calculate K_R for the reaction occurring in the calorimeter in the following manner. First, a K_R value is guessed and ΔH_{Ri} values for points at one-minute intervals along the thermometric titration curve are calculated. K_R is then varied until the function

$$U = \sum_{i=1}^n \left(\left\{ \left[\sum_{i=1}^n \frac{\Delta H_{Ri}}{n} \right] - \Delta H_{Ri} \right\}^2 |Q_{Ri} - Q_{Ri-1}| \right)$$

attains a minimum value where n is the number of data points taken and $|Q_{Ri} - Q_{Ri-1}|$ is a weighting factor. This weighting factor is necessary because the average mag-

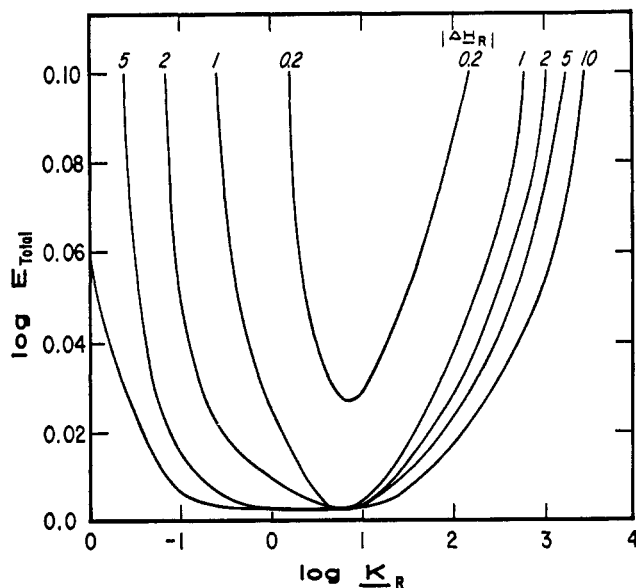


Figure 2. Plot of E_{total} vs. $\log K_R$

The $|\Delta H_R|$ value (kcal/mole) for the reaction is designated for each of the curves. $C_T = 0.5$.
Errors: $\pm 0.1\%$ in C_T , $\pm 0.1\%$ in C_S , and $\pm 0.4\%$ in Q_R

nitude of the error involved in reading Q_R is constant and independent of the magnitude of Q_R .

A slightly different method developed by Sillen (3) has also been used with good success to calculate equilibrium constants from calorimetric titration data (4). These calculations assign the "best" K and ΔH value(s) for the reaction(s) occurring in the calorimeter to be those which result in a minimum value in $U' = \sum_i [Q_i - Q_i(\text{calc})]^2$ where $Q_i(\text{calc})$

is a function of the K value(s), ΔH value(s), solution and titrant concentration(s), volume of solution, and volume of titrant added. The minimum value of U' is found by a "pit-mapping" routine (3, 4).

These two methods are similar, the main differences being the way in which the functions U and U' are minimized and in the weighting factor used in the calculation of U . A third method which has been used to calculate K and ΔH values from thermometric titration data (1, 2) involves solving for K and ΔH by taking all combinations of pairs of points and solving the equations rigorously rather than relying on a curve fitting procedure.

The entropy titration method has been successfully employed in the determination of $\log K$, ΔH° and ΔS° values for proton ionization (1, 2, 5-8), metal complexation (4, 9, 10), and donor-acceptor (11, 12) reactions.

The purpose of this paper is to define the optimum experimental conditions for the determination of equilibrium constants by the entropy titration method. Of the many variables which affect the accuracy of $\log K_R$ values, the most important are the experimentally measured heat values (corrected for chemical and nonchemical effects), Q_R ; the titrant concentration, C_T ; and the solution concentration, C_S . In this paper an analysis is made of the errors introduced in K_R when random errors of known magnitude are introduced into the Q_R , C_T , and C_S values, respectively.

CALCULATIONS

The reaction being considered is shown in Equation 1. The relationship between K_R and Equation 1 is given in Equation 4 where γ represents the activity coefficient of the subscripted species.

$$K_R = \frac{[A^-] \gamma_A - [HB] \gamma_{HB}}{[B^-] \gamma_B - [HA] \gamma_{HA}} \quad (4)$$

If the ionization constant and heat of ionization for HA are known, their contribution to K_R and ΔH_R can be calculated and subtracted to give K and ΔH values for Reaction 3 (see program 2, Appendix E of reference 7.) This approach is equally valid for cases involving different charges on the various species in solution and for different types of reactions.

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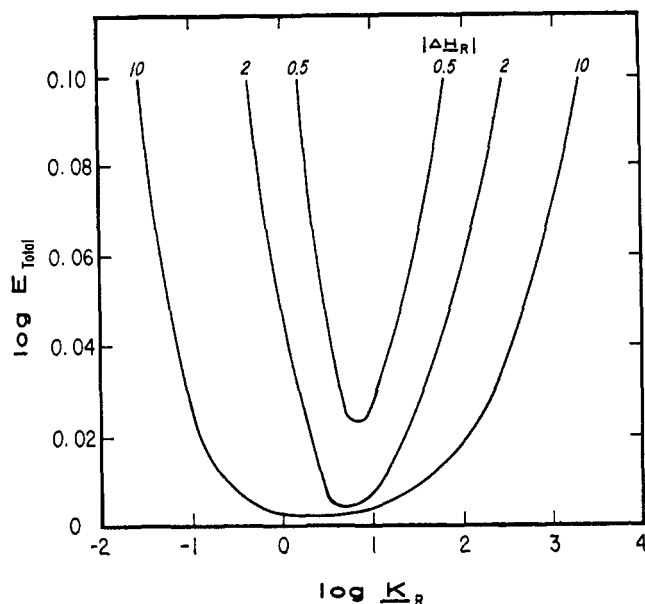


Figure 3. Plot of $\log E_{\text{total}}$ vs. $\log K_R$

The $|\Delta H_R|$ value (kcal/mole) for the reaction is designated for each curve. $C_T = 0.2$.

Errors: $\pm 0.1\%$ in C_T , $\pm 0.1\%$ in C_S , and $\pm 0.4\%$ in Q_R

The E_K values were determined in two steps. First, a computer program was written which generated Q_R values for given values of K_R , ΔH_R , C_T , C_S , volume of solution added, and volume of titrant added. (See program 1, Appendix E in reference 7.) In all calculations, the initial volume of the solution was set equal to 100 ml and the heat capacity of the calorimeter was set equal to 2 cal/deg. Eighteen Q_R values were calculated for each set of data corresponding to addition of 18 consecutive increments of titrant (0.34 ml per increment). For simplicity, it was assumed that the heat of ionization of HA and the heat of dilution of the titrant were zero. The titrant was assumed to be a solution of an acid. The Q_R values obtained from program 1, together with the corresponding C_T and C_S values, were then read into the entropy titration program (program 2, Appendix E in reference 7) and, in every case, the same K_R and ΔH_R value used to generate the Q_R values were calculated indicating that the program was functioning properly. Second, random errors of known magnitude (ΔQ_R , ΔC_T , ΔC_S) were introduced into the Q_R , C_T , or C_S values and $\log E_K$ was taken to be the absolute value of the difference between the $\log K_R$ values used to generate the Q_R values in program 1 and the $\log K_R$ value obtained from program 2 using $(Q_R + \Delta Q_R)$, $(C_T + \Delta C_T)$ or $(C_S + \Delta C_S)$ values. The ΔQ_R values were alternately taken to be either ± 0.0014 cal or $\pm 0.004 Q$ ($\geq 0.4\%$ error), whichever was greater. These ΔQ_R values were chosen to approximate the actual precision of existing thermometric titration equipment (13). The ΔC_T and ΔC_S values were set equal to $0.001 C_T$ and $0.001 C_S$ (0.1% errors), respectively. All calculations were performed on an IBM 7040 computer.

RESULTS

The $\log E_K(C_T)$ and $\log E_K(C_S)$ values were found to be equal and independent of C_T , C_S , and ΔH_R (for $|\Delta H_R| > 1$ kcal/mole). $\log E_K(C_T)$ and $\log E_K(C_S)$ are dependent on

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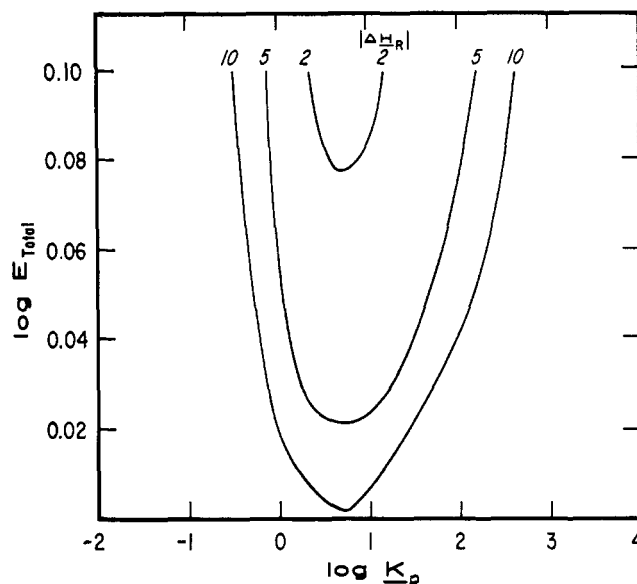


Figure 4. Plot of $\log E_{\text{total}}$ vs. $\log K_R$

The $|\Delta H_R|$ value (kcal/mole) for the reaction is designated for each of the curves. $C_T = 0.05$.

Errors: $\pm 0.1\%$ in C_T , $\pm 0.1\%$ in C_S , and $\pm 0.4\%$ in Q_R

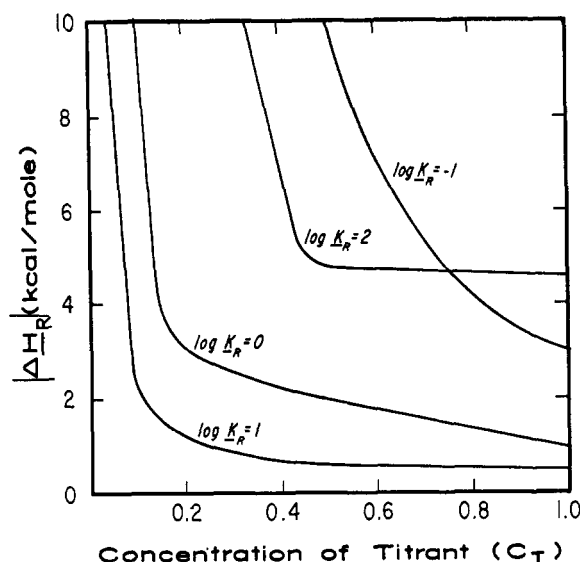


Figure 5. Plot showing combinations of C_T and $|\Delta H_R|$ values which result in a $\log E_{\text{total}}$ value = 0.01

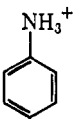


All combinations of C_T and $|\Delta H_R|$ values having coordinates above and to the right of the curve for a given $\log K_R$ value result in $\log E_{\text{total}}$ values less than 0.01

Errors: $\pm 0.1\%$ in C_T , $\pm 0.1\%$ in C_S , and $\pm 0.4\%$ in Q_R

$\log K_R$, and in Figure 1, $\log E_K(C_T) = \log E_K(C_S)$ values are plotted against $\log K_R$ to show this dependence.

The $\log E_K(Q_R)$ values are dependent on ΔH_R , K_R , C_T , and C_S . In order to reduce the number of variables to three, the ratio C_T/C_S was kept constant at 20 and approximately 300 $\log E_K(Q_R)$ values were calculated for various ΔH_R , K_R , and C_T values. Values for the overall variance in $\log K_R$ ($\log E_{\text{total}}$) defined as $[\log^2 E_K(C_T) + \log^2 E_K(C_S) + \log^2 E_K(Q_R)]^{1/2}$ were calculated for the 300 combinations of ΔH_R , K_R , and C_T . These $\log E_{\text{total}}$ values are plotted vs. $\log K_R$ with ΔH_R as the third parameter in Figures 2, 3, and 4 for C_T values of 0.5, 0.2, and 0.05, respectively.

Table I. Suggested Titrants ($\text{HA} = \text{A}^- + \text{H}^+$)

| Effective pK range | Substance | Formula | pK | ΔH° (kcal/mole) |
|--------------------|----------------------------------|---|-----------------|------------------------------|
| <2.5 | Hydrogen ion | H_3O^+ | ≤ 1 | 0 |
| | Hydrazinium (+2) ion | $\text{N}_2\text{H}_6^{2+}$ | -0.67 (7) | 8.9 (7) |
| 1-4 | Phosphoric acid | H_3PO_4 | 2.148 (14) | -1.88 (15) |
| 3-6 | Anilinium ion |  | 4.60 (16) | 7.28 (16) |
| 4-7 | Acetic acid | CH_3COOH | 4.756 (17) | -0.01 (8) |
| | Pyridinium ion |  | 5.17 (8) | 4.98 (8) |
| 6-9 | Dihydrogen phosphate ion | H_2PO_4^- | 7.198 (18) | 0.90 (19) |
| | Imidazolium ion |  | 6.99 (8) | 8.78 (8) |
| 8-11 | Acetylacetone | $\text{CH}_3\text{COCH}_2\text{COCH}_3$ | 9.02 (20), (20) | 2.8 (20) |
| | Tris(hydroxymethyl)amino methane | $(\text{CH}_2\text{OH})_3\text{CNH}_3^+$ | 8.069 (27) | 11.33 (21) |
| 9-12 | Glycinium ion | $^+\text{H}_3\text{NCH}_2\text{COO}^-$ | 9.780 (22) | 10.57 (23) |
| 11-14 | Monohydrogen phosphate ion | HPO_4^{2-} | 12.39 (2) | 4.20 (2) |
| | Hydroxide ion | OH^- | 13.998 (24) | 13.335 (25) |

For convenience, the $E_K(Q_R)$ values are presented in a somewhat different form in Figures 5 and 6. For the designated $\log K_R$ value, each of the curves in Figure 5 corresponds to a $\log E_{\text{total}}$ value of 0.01, while those in Figure 6 correspond to a $\log E_{\text{total}}$ value of 0.05. Thus, any combination of C_T and ΔH_R values having coordinates above and to the right of the curve will result in a $\log E_{\text{total}}$ value of less than 0.01 in Figure 5 or 0.05 in Figure 6. For example, if the pK value to be determined is about 6, one could titrate a solution of pyridinium ion ($\text{pK} = 5$) into a solution of the ionized form of the compound so that the $\log K_R$ value for the reaction occurring in the calorimeter would be +1. Then a titrant concentration of 0.2F (Figure 5) could be used to determine the pK value to an accuracy of better than 0.01 pK unit as long as $|\Delta H_R| > 1$ kcal/mole. $\log E_{\text{total}}$ is independent of the sign of ΔH_R .

DISCUSSION

The entropy titration method is most effective when the $\log K_R$ value is 0.7 ± 0.1 . (See Figures 2-4.) However, the $\log K_R$ value for any reaction for which $|\Delta H_R| > 5$

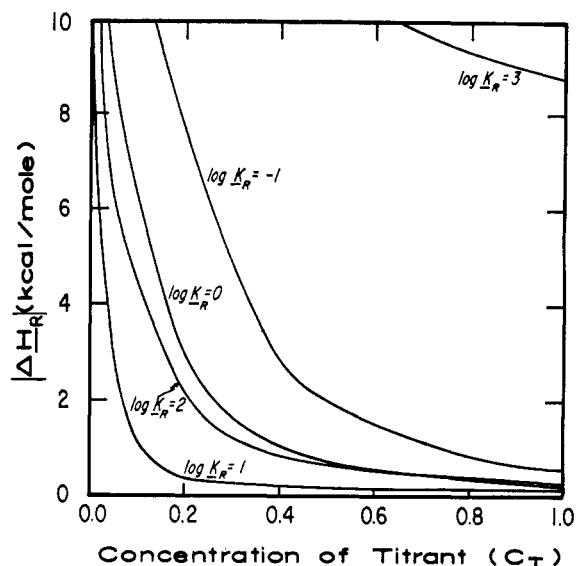


Figure 6. Plots showing combinations of C_T and $|\Delta H_R|$ values which result in a $\log E_{\text{total}}$ value of 0.05

All combinations of C_T and $|\Delta H_R|$ values having coordinates above and to the right of the curve for a given $\log K_R$ value result in $\log E_{\text{total}}$ values less than 0.05.

Errors: $\pm 0.1\%$ in C_T , $\pm 0.1\%$ in C_S , and $\pm 0.4\%$ in Q_R

kcal/mole can be determined with an accuracy of ± 0.01 $\log K$ unit if $-1 < \log K_R < 2$ (see Figure 5), assuming the random errors in C_T , C_S , and Q_R are not larger than 0.001 C_T , 0.001 C_S , and 0.004 Q_R , respectively. Although the magnitude of the effect on $\log E_{\text{total}}$ of increasing the ratio C_T/C_S was not specifically calculated in the study, increasing C_T/C_S will slightly improve the accuracy of the entropy titration method when $\log K_R < 0.7$ and will slightly decrease the accuracy when $\log K_R > 0.7$.

Through the proper choice of titrant, the pK value for proton dissociation in aqueous solution for any species can

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be accurately determined by this method, as long as the pK and ΔH values for proton dissociation from the acid constituent of the titrant are well known. This has been demonstrated (8) using an acetic acid ($pK = 4.8$) solution as titrant. The choice of titrant is dictated by the pK and ΔH° values of the substance to be studied. In Table I are listed substances which may be used to accurately determine any pK values less than 15 and greater than -1 .

Since it is desirable to have $|\Delta H_R^\circ|$ for the reaction occurring in the calorimeter as large as possible, two titrants of quite different ΔH° values are suggested in Table I for each pH range.

Once the pK value has been determined by the entropy titration method, it can be used to calculate ΔH and ΔS values for the reaction from the same thermometric titration

data (2). Recently, Cabani and Gianni (26) have also evaluated the entropy titration method with somewhat pessimistic conclusions concerning the calculation of equilibrium constants by this method. However, the errors assumed by these authors are large compared to those assumed in the present work or which might be expected with available equipment.

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Determination of Linear 1-Chloroalkanes in Mixtures of Linear and Nonlinear (C_{12} – C_{16}) Chloroalkanes by Reaction Kinetics

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A method to determine the linear 1-chloroalkanes in mixtures of C_{12} – C_{16} chloroalkanes is presented. Controlled amination with piperidine results in 99+%, 54%, and 1.3% of linear 1, β -branched, and internal chloroalkanes, respectively, after 120 minutes. Specific reaction rate data are presented to allow differentiation of the linear 1, and nonlinear chloroalkanes with moderate accuracy in the system. Total chloride is determined by decomposition to inorganic chloride.

DETERMINATION of organic halogen has been described by many workers. For example, total halogen requires total decomposition to an ionizable moiety and subsequent conventional halide titration (1).

Relative reaction rates of primary and secondary as well as isomeric low molecular weight pure organic halides have also been described (2–8). It was observed that relative reaction rates between primary and secondary organic halides were quite different. Too, the pure low molecular weight isomeric organic halides studied by Mark *et al.* (7) showed a significant difference in reaction rate between normal and isopropyl organic halides. However, little is known about the relative reaction rates of high molecular weight ($>C_{12}$) isomeric mixtures, although it can be postulated that they will differ significantly and serve as a basis for analytical separa-

tion. Further, from C_{12} to C_{16} the difference in relative reaction rates between homologs of linear and nonlinear moieties should be essentially insignificant.

It was desirable to determine the linear 1-chloroalkane in the presence of relatively small amounts of β -branched chloroalkane, and $<2\%$ internal chloroalkane, all in the C_{12} – C_{16} range. The work described here demonstrates the separation and quantization of linear 1-chloroalkane in the presence of other chloroalkane in mixtures by controlled dehydrochlorination with piperidine under carefully controlled conditions.

The primary requirement of this work was differentiating a very high concentration ($>95\%$) of linear 1-chloroalkane in the presence of minor concentrations of nonlinear branched and/or internal chloroalkanes in C_{12} – C_{16} matrices. The reaction rate for each moiety differs enough so that the linear concentration can be determined by applying a calculation similar to the method of proportional equations described by Garmon and Reilley (9).

Briefly, the chloroalkane mixture is reacted at steam bath temperatures with a large excess of piperidine in 9:1 N,N' -dimethylformamide–water solvent until the linear 1-chloroalkane is 99+ % reacted (120 minutes). From known kinetic studies of pure linear 1-chloroalkane and nonlinear β -branched chloroalkanes, as well as total chloride by total decomposition, the linear 1-chloroalkane can be calculated. Nonlinear chloroalkane (including any internal chloride) is then determined by difference.

EXPERIMENTAL

Apparatus and Reagents. Titrations were carried out using a Sargent Model D automatic recording titrator and a Pt–Pt electrode couple.

Two-ounce glass bottles with rubber-lined screw caps and other suitable glassware, steam bath, etc., were used.

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