Standard Errors and Confidence Intervals in Nonlinear Regression: Comparison of Monte Carlo and Parametric Statistics

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A Monte Carlo method is employed to characterize distributions of parameter values calculated in nonlinear regression problems. Accurate estimates of confidence intervals are easily obtained. Two illustrative numerical examples are provided to compare the Monte Carlo uncertainty estimates with those derived by use of standard methods of parametric statistics. The customary assumptions that (1) the effects of covariances between pairs of the parameters can be ignored and (2) that the distributions of the parameters are normal are shown to lead to significant errors, up to 2- and 3-fold in the calculated uncertainties. The Monte Carlo method is free from these assumptions and their associated errors.

Introduction

Methods for the calculation of adjustable parameters in both linear and nonlinear regression problems have been extensively discussed.1-3 Less attention has been paid to the calculation of the uncertainties in the optimized values of these parameters. Difficulties arising from nonnormal distributions of adjustable parameters calculated in nonlinear regressions and from the existence of errors in both dependent and independent experimentally determined quantities as well as errors in fixed quantities are often ignored. Finally, the interdependencies among the calculated parameters are generally not considered. As a consequence, standard error estimates and the confidence intervals obtained by conventional nonlinear regression methods are sometimes incorrect.

These difficulties can all be overcome by using a Monte Carlo simulation method.4 As will be shown below, the Monte Carlo method is extremely simple to implement. Because of its simplicity and because the method is essentially a realization of the definition of random errors in terms of many hypothetical repetitions of the entire experiment, the Monte Carlo method is highly intuitive. As such it provides a useful and accurate means of estimating statistical uncertainties in nonlinear regression problems.

The General Regression Problem

In a general regression problem ideal data, subject to neither systematic nor random error, are presumed to satisfy exactly an equation of the form

\[ F(q_1, q_2, \ldots, q_r, \alpha_1, \ldots, \alpha_s, \beta_1, \ldots, \beta_l) = 0 \]  

(1)

\( F \) is a function of the \( n \) different measured properties \( q_i \), the \( r \) parameters \( \alpha_i \) whose values are initially unknown, and the \( s \) parameters \( \beta_i \) whose values are assumed to be known. The sought for \( \alpha_i \) parameters are adjusted until (1) is satisfied exactly. The values of the \( r \) parameters \( \alpha_i \) represent solutions to the regression problem.

Essentially the same procedure is employed to evaluate real experimental data where each of the measured properties \( q_i \) and "known" parameters \( \beta_i \) is subject to random error. We will assume throughout this work that systematic errors are not present. Measured \( q_i \) values are substituted into (1), and the values of the \( \alpha_i \) parameters are adjusted to obtain a "best fit" of the equation to the data. Because random errors are present in the \( q_i \) and \( \beta_i \), the equation is now only approximately satisfied. Adjustment of the values of the \( \alpha_i \) to obtain the best fit is accomplished by a least-squares procedure. First, it is assumed that one of the measured properties, here denoted by \( q_i \), can be expressed as an explicit function of the other measured properties and the parameters \( \alpha_i \) and \( \beta_i \). Second, it is assumed that the values of the remaining \( q_i \) and of the \( \alpha_i \) and \( \beta_i \) parameters are taken to be error free so that only \( q_i \) suffers an error. We have

\[ q_i + \varepsilon_i = Q_i = f(q_{j1}, q_{j2}, \ldots, q_{jk}, \alpha_1, \ldots, \alpha_s, \beta_1, \ldots, \beta_l) \]  

(2)

where \( Q_i \) is the value of property \( q_i \) calculated from the explicit function \( f \). Its value differs from the observed \( q_i \) by a random error \( \varepsilon_i \), whose expectation value \( \langle \varepsilon_i \rangle \) is 0 and whose variance is \( \sigma(q_i)^2 \). It is also necessary to assume that when the experiment is repeated using different sets of values of the independent variables, the values of \( \varepsilon_i \) for each \( q_i \) are independent of each other. It is not necessary to assume that \( \varepsilon_i \) is a normally distributed variable, but only that its variance is finite. The assumption of normality is required only for the construction of confidence intervals.

The least-squares criterion for the best fit is realized by minimizing \( \chi^2 \) (chi-square), where

\[ \chi^2 = \sum_{j=1}^{N} \left[ \frac{q_{ij} - Q_{ij}}{\sigma(q_{ij})} \right]^2 \]  

(3a)

\[ = \sum_{j=1}^{N} \left[ \frac{q_{ij} - Q_{ij}}{\sigma(q_{ij})} \right]^2 \]  

(3b)

In these equations, the sum is over \( N \) sets of experimental data indexed by \( j \). Each set consists of \( n \) measurements of the properties \( q_i \). Thus, \( q_{ij} \) represents the value of \( q_i \) observed during the \( j \)th experiment and \( [\sigma(q_{ij})]^2 \) is the variance of \( q_{ij} \).

Minimization of \( \chi^2 \) may be accomplished analytically when \( f \) is a linear function of the adjustable parameters. An example is the well-known weighted least-squares linear regression. Dependent \( y \) values are taken to be error free that may vary from one measurement to the next, while independent \( x \) values \( (q_{ij}) \) are taken to be exact. Best values of slope and intercept \( (a_0 \text{ and } a_1) \) are analytical functions of the \( q_{ij} \) and \( q_{ij}^2 \). Variances of the slope and intercept are readily derived in closed form.

If the functional form of (2) is nonlinear in the adjustable parameters and if, once again, there are errors only in the dependent variables \( q_{ij} \), then the Levenberg–Marquardt method provides an efficient iterative algorithm for determining best fit values of the adjustable parameters and their variances.4,9 In
either case, if the functional form of (1) and (2) accurately represents the interrelationship of the data and the adjustable and fixed parameters, and if \( (\sigma(q_{ij}))^2 \) has a fixed (i-independent) value, then the value of \( \chi^2 \) can be approximated by \( \chi^2 \sim N - r \), the number of degrees of freedom. Moreover, the best fit values of \( a_i \) represent the maximum likelihood values of these parameters. We defer the discussion of variance estimates and confidence intervals for the optimized values of \( a_i \) to a later section.

If the simplifying assumptions mentioned above are not satisfied, the problem becomes much more difficult. Nevertheless, methods for evaluating the optimized values of the parameters are by now well established and can be implemented by suitable modifications in the Levenberg–Marquardt procedure.

**Extension of the Levenberg–Marquardt Method**

The extension of the Levenberg–Marquardt method involves three steps:

1. If the model function is defined implicitly, it can be converted to an explicit form using numerical methods. One of the variables, say \( q_i \), is arbitrarily chosen to be dependent. Given the values of all the other \( q \)'s and the fixed and adjustable parameters, (1) can be solved numerically for \( q_i \). The derivatives of \( q_i \) with respect to each adjustable parameter \( a_i \) and with respect to the other \( q \)'s can be evaluated by use of standard techniques of calculus for implicit differentiation.

2. Because there are errors in each of the independent variables and in each of the fixed parameters, \( \sigma(q_{ij}) \) must be replaced by

\[
\sigma_j^2 = \sigma(q_{ij})^2 + \sum_{i=1}^{n} \left( \frac{\partial F}{\partial a_i} \right)^2 \sigma(a_i)^2 \sum_{i=1}^{n} \left( \frac{\partial F}{\partial q_{ij}} \right)^2 \sigma(q_{ij})^2
\]

(4)

3. Finally, as Jefferys points out, all the derivatives used in the procedure should be evaluated by using the best estimates of the data points as well as the best estimates of the parameters rather than simply at the observation points.\(^{11}\) Assuming two measured properties only, \( x \) an independent variable and \( y \) the dependent one, the correction \( \delta x \) to the observed value of \( x \) is given by

\[
\delta x = \frac{\sigma_y^2 (y - \bar{y}) \left( \frac{\partial y}{\partial x} \right) + \sigma_x^2 (x - \bar{x})}{\sigma_y^2 \left( \frac{\partial y}{\partial x} \right)^2 + \sigma_x^2}
\]

(5)

where \( x \) and \( y \) are the measured points, \( \bar{x} \) is the present best guess of the corrected value of \( x \), and \( y \) is the value of the model function calculated at the best present values of \( x \) and of the other parameters. Note that if there is no error in \( x \), the correction is zero.

Examples of the implementation of points 1 and 2 are given by Wentworth,\(^{24}\) implementation of point 3 for linear regression problems is given by Lybanon.\(^{12}\)

**Standard Errors of the Parameters**

The customary method for obtaining the uncertainties in each of the optimized values of the adjustable parameters involves inverting the matrix \( A \) whose \( kth \) element is given by

\[
A_{kl} = \frac{\sum_{j=1}^{n} \left( \frac{\partial q_{ij} \cdot \partial a_k}{\partial a_l} \right) \left( \frac{\partial q_{ij} \cdot \partial a_l}{\partial a_k} \right)}{\sigma_j^2}
\]

(6)

where \( q_{ij} \) denotes the \( jth \) measurement of the \( n - 1 \) \( q_i \)'s chosen to be the independent variables and \( k \) denotes the set of the \( r \) adjustable parameters. The diagonal element \( C_{ii} \) of the covariance matrix \( A^{-1} \), called the covariance matrix, is the variance, i.e., the second central moment, of the parameter \( a_i \). In most treatments of this subject it is maintained that the square root of \( C_{ii} \) or \( \sigma(a_i) \), is the standard error of \( a_i \) with the implication that there is a 68.3% probability that the “true” value of \( a_i \) lies in a (confidence) interval of width \( 2\sigma(a_i) \). However, the square root of the variance is the standard error only if each adjustable parameter \( a_i \) can be considered to be drawn from a Gaussian distribution. In other words, if the experiment were repeated many times, each repetition would yield a value of \( a_i \) and the set of these \( a_i \) would be distributed normally.

In general we have no reason for assuming that the parameters are distributed normally. A normal distribution of each of the adjustable parameters depends on the following conditions: (1) The errors in the data must be normally distributed. (2) The mathematical model must be expressed as a function linear in the adjustable parameters and linear in the data variables. If these conditions are satisfied, the optimized values of the adjustable parameters can be expressed as linear functions of the data points. Since linear functions of normally distributed variables are also normally distributed, the adjustable parameters are themselves normally distributed.

These conditions are satisfied for only the simplest textbook examples of linear and multiple linear regression. For these special cases, the square root of the diagonal matrix element \( C_{ii} \) is the standard error of \( a_i \) and confidence intervals can be calculated by using values of Student’s \( t \) or the multivariate \( F \) statistic.\(^{13-15}\) Note that if the model equation has been transformed from a nonlinear to a linear form, then the errors of the transformed variables must be normally distributed, if the adjustable parameters are also to be normally distributed.

Even if the distribution of the adjustable parameters is normal, the standard error estimate derived from the diagonal matrix element \( C_{ii} \) of the covariance matrix does not necessarily reflect the uncertainty in \( a_i \). The off-diagonal elements \( C_{ij} \) are the covariances of \( a_i \) and \( a_j \), which are generally nonzero. The standard error estimate for a particular \( a_i \) obtained from the square root of the \( C_{ii} \) matrix element depends on the assumption that the other parameters are fixed at their optimized values.

Bard\(^{16}\) and more recently Schwartz\(^{14}\) have developed ad hoc methods for approximating joint confidence intervals for multiparameter regression analysis. Their methods rely on the assumption that calculated \( a_i \) values are normally distributed, a condition that we have seen is generally not realized. Furthermore, the procedures suggested by these authors do not provide probabilistic interpretations of the approximate confidence intervals. We show below that the Monte Carlo method does provide such probabilistic interpretations.

**Monte Carlo Calculation of Confidence Intervals**

The Monte Carlo method of calculating the errors in the adjustable parameters overcomes all of the difficulties discussed in the previous section. An implementation of the procedure consists of the following steps:

1. Compute the optimized values of \( a_i \) using the extended Levenberg–Marquardt method.

2a. Simulate a repetition of the experiment by generating a new set of \( q_{ij} \) and \( \beta \) such that

\[
q_{ij} = q_{ij} + \epsilon_i
\]

(7a)

and

\[
\beta_j = \beta_j + \epsilon_j
\]

(7b)

where \( \epsilon_i \) and \( \epsilon_j \) are random variables chosen to approximate uncertainties in \( q_{ij} \) and in \( \beta \). We employ the Box–Muller method to provide random Gaussian-distributed values with mean zero and appropriate standard deviation for \( \epsilon_i \) and \( \epsilon_j \).\(^{16}\) If \( x \) is the Gaussian-distributed variable with mean \( \mu \) and variance \( \sigma^2 \), then

\[
\mu + \frac{\sigma}{\sqrt{2\pi}} \exp\left(-\frac{1}{2} \left(\frac{x - \mu}{\sigma}\right)^2\right)
\]

is a normal distribution with mean \( \mu \), variance \( \sigma^2 \), and standard deviation \( \sigma \).
\[ x = z \sigma + \mu \]  
\[ z = (-2 \ln (p_1))^{1/2} \cos 2 \pi p_2 \]

In (9), \( z \) is a normally distributed variable (mean = 0; variance = 1), while \( p_1 \) and \( p_2 \) are uniformly distributed random numbers between 0 and 1.

It should be noted that other distributions, perhaps better suited to the data in question, could be used to generate the new set of \( q_i' \) and \( b_i' \). However, alternative error distributions must be consistent with the least-squares best fit conditions which is inherent in regression analysis. That is, both \( e_i \) and \( e_i' \) must have expectation values of zero and have finite variances.

3. Step 2 is now repeated many times. The set of calculated \( A_i \) values constitutes by definition the distribution function for each \( a_i \).

At this point we note a most convenient property of the Monte Carlo method. It is frequently the case that a sought-for parameter is a function of two or more \( a_i \) parameters. A classic example is found in determining the \( pK \) for an indicator by spectrophotometric measurement. A plot of reciprocal absorbances versus \( 1/[H^+] \) provides slope and intercept values whose ratio is interpreted in terms of the indicator constant. The Monte Carlo method allows direct calculation of this ratio of the \( A_i \) values arising from the corresponding \( a_i \) parameters and thus provides the distribution of this ratio. This procedure automatically accounts for interdependencies (covariances) between \( a_i \) values.

The values of \( A_i \) and any other calculated parameters which are functions of the \( A_i \) are now sorted in numerical order. Standard error estimates are here defined as 68.3% confidence intervals. The number of Monte Carlo simulations is chosen to be sufficient large so that the Student's \( t \) statistic is essentially 1.00 at the 68.3% confidence level. The confidence intervals are obtained from the ordered list by eliminating from the list those \( A_i \) values included in the upper and lower 15.8% \((100 - 68.3)/2\) of values. In the same manner, 90% confidence intervals correspond to the range of parameter values that remain after the exclusion of the upper and lower 5% of the values. This procedure obviates the need for the frequently encountered assumption that the values of \( a_i \) parameters are distributed normally and for the assumption that the experimental uncertainties \( e_i \) be small compared with the measured quantities \( q_i \).

**Examples**

We illustrate the Monte Carlo procedure using two examples. The first involves an analysis of kinetic data provided by Wentworth in an often quoted paper. The second calculates the equilibrium constant in a hypothetical dimerization reaction.

### Decomposition of Acetaldehyde

Wentworth describes an experiment in which the rate constant and reaction order for the decomposition of acetaldehyde into methane and carbon monoxide is determined by measuring the total pressure of the gaseous mixture \( P \) in millimeters as a function of time \( t \) measured in seconds. The initial value of the pressure is \( P_0 \) at time zero. The reaction order is \( n \) and the model equation is

\[ -(2P_0 - P)^{n+1} + (n - 1)kt + P_0^{n+1} = 0 \]

In (10) \( P_0 \), \( n \), and \( k \), the rate constant, are taken as adjustable parameters. The data are reproduced in Table I. We follow Wentworth in assuming normally distributed errors in \( P_t \) and \( t \), with \( \sigma(P_t) = 1.0 \text{ mm} \) and \( \sigma(t) = 1.0 \text{ s} \).

Using the extended Levenberg–Marquardt method, we obtain the parameter values also shown in Table I. These values are close to those found by Wentworth. The two methods differ most in calculating the rate constant, \( k \), which is estimated as 7.153 \times 10^{-6} \text{ by Wentworth and here as 7.454 \times 10^{-6}}. We conclude that the Jefferys correction employed in the present calculation has only a minor effect. The \( \chi^2 \) statistic, found to be 2.42, is in good agreement with the number of degrees of freedom \((N - r = 7 - 3)\).

Wentworth obtains standard error estimates for each adjustable parameter by taking the square root of the appropriate diagonal element of the covariance matrix. He finds 1.00, 0.0259, and 1.065 \times 10^{-4} for standard errors in \( P_0 \), \( n \), and \( k \), respectively. The Levenberg–Marquardt algorithm also provides uncertainties based on the diagonal elements of the covariance matrix. The values obtained from this algorithm are similar to Wentworth’s. We employ these standard error estimates obtained from the covariance matrix to obtain the 68.3% and 90% confidence intervals for the three adjustable parameters. For each \( a_i \), these intervals extend \( t a_i \) above and below the mean value \( a_i \), where \( t \) is the Student’s \( t \) statistic. For the present case of four degrees of freedom, \( t \) is equal to 2.13 for the 68.3% and 90% confidence intervals, respectively. We note that this procedure relies on the customary assumption of normally distributed \( a_i \).

The confidence interval half-widths \( t a_i \) are to be compared with those obtained from the Monte Carlo values, based on 200 hypothetical repetitions of the experiment, shown in Table I. These results indicate relatively minor differences in the confidence intervals but predict significantly different 90% intervals. For example, the 68.3% half-interval for \( n \) based on the extended Levenberg–Marquardt solution and employing the standard error derived from the covariance matrix is 0.028. That is, the “true” value of \( n \) lies in the interval 1.948 \leq n \leq 2.004 with 68.3% confidence. The corresponding Monte Carlo estimate of the half-width is 0.025, implying a 68.3% confidence interval of 1.951 \leq n \leq 2.001. The 90% confidence half-width estimates are 0.054 and 0.036, based on the covariance matrix and on Monte Carlo calculations, respectively. Expressed as percent differences, the 68.3% and 90% confidence intervals for the parametric calculations differ by about 10% and 50% from the corresponding Monte Carlo calculations, respectively. These estimates, especially for the 90% confidence intervals, appear to be significantly different.

We note that the estimates based on the covariance matrix are too conservative compared with the Monte Carlo results. The joint parametric uncertainty estimates using the method suggested by Schwartz are even more conservative; they are about a factor of 3 larger than \( t a_i \).

The agreement for the 68.3% confidence interval is a result of two factors. First, the distributions of \( P_0 \), \( n \), and \( k \) are well approximated by a Gaussian distribution with a variance given by the diagonal elements of the covariance matrix in the central region (defined by the 68.3% confidence interval). This situation obtains in many problems, such as those discussed by Schwartz, where the experimental errors are sufficiently small so that the

**Table I: Decomposition of Acetaldehyde**

<table>
<thead>
<tr>
<th>( P_0 ), mmHg</th>
<th>( n )</th>
<th>( 10^4 k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>364.08 ± 1.00</td>
<td>1.963 ± 0.0259</td>
<td>7.153 ± 1.065</td>
</tr>
<tr>
<td>363.95 ± 0.997</td>
<td>1.976 ± 0.0252</td>
<td>7.454 ± 1.090</td>
</tr>
</tbody>
</table>

**Confidence Intervals**

<table>
<thead>
<tr>
<th>Wentworth</th>
<th>Levenberg–Marquardt</th>
<th>Monte Carlo</th>
</tr>
</thead>
<tbody>
<tr>
<td>68.3%</td>
<td>90%</td>
<td>68.3%</td>
</tr>
<tr>
<td>0.029</td>
<td>0.055</td>
<td>0.028</td>
</tr>
<tr>
<td>0.054</td>
<td>0.036</td>
<td>0.025</td>
</tr>
</tbody>
</table>

The confidence interval half-widths have been calculated using the standard error estimates obtained from the extended Levenberg–Marquardt solution.
distribution in the central region is approximately Gaussian. Second, the agreement in this example depends on the fact that the covariances between pairs of the adjustable parameters are small and, moreover, have different signs and thus tend to cancel.

The lack of agreement between the Wentworth and Monte Carlo calculation for the 90% confidence interval indicates that the distribution of the parameters cannot be approximated by a Gaussian distribution if the "tails" of the distribution are important in the calculation of the interval. In the Wentworth example, the adjustable parameters have distributions that decay more steeply than does the Gaussian.

2. Hypothetical Spectrophotometric Analysis of a Dimerization Equilibrium. In the second example, we envision a series of 10 spectrophotometric measurements recording absorbances, A, using a path length b cell with solutions of differing concentration, C of some substance which undergoes dimerization. Extinction coefficients for the monomer and dimer are $a_M$ and $a_D$, respectively. The dimer dissociation constant is $K$. The model equation is

$$A = b(a_M - a_D/2)|M| + b a_D C/2 \quad (11)$$

where

$$|M| = [-K + (k^2 + 8CK)^{1/2}]/4$$

Idealized A versus C data are obtained from (11) and (12) using $0.003 \leq C \leq 0.1; K = 0.03; a_M = 20.0; a_D = 2.00$; and $b = 1.00$. The measured quantities, $A$ and $C$, are then subjected to experimental error by randomly perturbing their values using the Box–Muller method and arbitrarily taking $\epsilon_A$ and $\epsilon_C$ to be equal to 0.0005 and 0.0003, respectively. In this way we avoid the possibility of systematic errors in the following analysis. We assume that $b$ is error-free. Randomly perturbed $A$ and $C$ data, shown in Table II, are now fit to the model equation by the extended Levenberg–Marquardt algorithm with results also given in Table II. The goodness-of-fit parameter, $\chi^2$, had a value of 4.9, reasonably close to the 7 degrees of freedom. The calculated $K$, $a_M$, and $a_D$ values approximate their "true" values.

Standard error estimates from diagonal elements of the covariance matrix are listed along with confidence intervals based on $t = 1.06$ and 1.99 for 68.3% and 90% confidence levels, respectively. Monte Carlo confidence intervals, obtained from 200 simulations, for the three adjustable parameters are 2–3 times smaller than those obtained from the diagonal elements of the covariance matrix. That is, the Monte Carlo simulation indicates that the $A$ versus $C$ data determine the values of the adjustable parameters with a much higher precision than the usual methods of uncertainty estimation would indicate.

We attribute the differences between the error estimates obtained from the two methods, even at the 68.3% confidence level, principally to significant covariances between parameters rather than to deviations from parameter normal distributions. We have seen earlier that the effects of non-normal parameter distributions are minor at the 68.3% confidence level in problems such as these where the experimental errors are small. In the present example, standard error estimates from diagonal elements of the covariance matrix neglect the interdependencies between parameters and lead to erroneous results. We note that one cannot conclude that confidence intervals based on the covariance matrix will always be too conservative. In other problems the parameter covariances could be such that estimates based on the covariance matrix would be too optimistic.

Both the parametric and Monte Carlo error analyses rely on accurate estimates of the uncertainties in the measured quantities (concentrations and absorbances in this example). In many practical applications such estimates may not be available. In such cases the $x^2$ statistic obtained in the fitting procedure provides some information. Suppose that the uncertainty in one of the measured quantities (perhaps in the concentration) is known. The error in the other quantity (absorbance) can then be estimated by choosing its value so that $x^2$ becomes approximately equal to the number of degrees of freedom. In the two examples, the values of $x^2$ differ from the number of degrees of freedom by approximately 40% and 30%, respectively. Using (3b) and assuming for simplicity that all the $\sigma(q_i)$ are equal, we find that the errors in the estimates of the $\sigma(q_i)$ are probably no greater than 20%. This procedure of course assumes that the mathematical model describing the experiment is correct. While this approach has often been employed in estimating experimental uncertainties, it seems inferior to the traditional "experimental" method of simply repeating a given measurement an appropriate number of times.

### Practical Considerations

How many times should the Monte Carlo simulation be repeated? In an effort to answer this question we determined confidence intervals of the adjustable parameters derived in the dimerization equilibrium problem using 60, 100, 200, and 400 repetitions. The results of these calculations appear in Table III. They indicate that, at least for this example, essentially constant estimates of the confidence intervals are obtained after only 60 repetitions. These results are not unreasonable since each Monte Carlo simulation involves an average over 20 random variables (10 absorbances and 10 concentrations). The adjustable parameters are in a sense mean values derived from the data, so that the random fluctuations in the data points tend to cancel.

There do exist theoretical estimates, such as the Chebychev inequality and estimates based on the central limit theorem, of the number $L$ of Monte Carlo simulations required for a particular problem. We believe that the most practical means of determining $L$ in the problem of determining confidence intervals is to note that if the confidence intervals derived from $L$ and from $2L$ simulations are reasonably similar, these intervals are quite probably accurate estimates of the "true" confidence intervals. The number of simulations required to determine the 90% confidence interval is naturally larger than the number needed for the 68.3% since the 90% interval relies on the relatively few number of extreme $q_i$ values. A prudent course involves choosing $L$ large enough so that at least 5–10 extreme $q_i$ values from each side of the distribution are discarded. This corresponds to $L > 30$ for the 68.3% interval and $L > 100$ for the 90% interval. A repetition of the calculation with $2L$ simulations can then be
Radiolytic Generation of Organic Radical Cations in Zeolite Na–Y

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Several examples of radiolytically generated organic radical cations in zeolite Na–Y are illustrated. EPR studies of organic radical cations can be carried out over a wide range of temperatures up to room temperature. In every case, monomeric radical cations were observed. Comparison to previous work in freon and xenon matrices is made, illustrating that in the zeolite Na–Y there is considerably weaker radical cation–matrix interaction. A mechanism of radiolytic generation of radical cations in zeolite Na–Y is proposed.

Introduction

The study of organic radical cations is closely tied to the methods that allow their preparation and stabilization. In the past decade, many organic radical cations have been examined by EPR and optical absorption spectroscopy using low-temperature halocarbon solvents.1 With smaller organic cations, the more inert neon matrix was successfully utilized.2 Recently, we have found that xenon matrices can be used to study organic radical cations by EPR over a considerable temperature range.3 A recent report has illustrated how superacidic membranes such as Nafion can be used to stabilize and study radical cations, even at room temperatures.4

In order to stabilize organic radical cations, two dominant processes must be prevented. First, we must prevent the reverse electron transfer when the electron, ejected from the neutral to give the radical cation (eq 1), returns to neutralize the radical cation (eq 2).

\[
\begin{align*}
\text{RH} & \xrightarrow{h\nu} \text{RH}^+ + e^- \\
\text{RH}^+ + e^- & \rightarrow \text{RH}^* 
\end{align*}
\]

(1) (2)

This is accomplished by scavenging the electron and preventing the possibility of back electron transfer as in halocarbons, where dissociative electron capture (eqs 3 and 4) takes care of the electron permanently.

\[
\begin{align*}
e^- + \text{RCI} & \rightarrow \text{RCI}^- \\
\text{RCI}^- & \rightarrow \text{R}^* + \text{Cl}^-
\end{align*}
\]

(3) (4)

The second reaction we must prevent is an ion–molecule reaction of the radical cation. Several dominant radical cation reactions

\begin{itemize}
\end{itemize}