EFFECT OF PRESSURE ON THE BROMINATION OF RING-SUBSTITUTED TOLUENES BY N-BROMOSUCCINIMIDE

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Radical substitution studies [1-4] have shown that the effect of pressure in increasing the rates of \[ \text{R} + \text{H} - \text{C} = \text{R-H} + \text{C} - (\text{R=C, Cl, Br}) \] reactions is more pronounced the higher the reaction rate constant at atmospheric pressure. In many cases, including the bromination of hydrocarbons by N-bromosuccinimide (N-BSI), the logarithm of the rate constant ratio proves to be a linear function of the difference in the activation volume effects (AVE) accompanying substitution. An exception here is the bromination of m-bromotoluene by N-BSI [4]. This has led to the study of the effect of pressure on the bromination of certain ring substituted toluenes. A brief report of the results of this study has appeared in [5]. The present paper will give more detailed data on the radical-chain bromination of substituted toluenes by N-BSI in CH\(_2\)Cl\(_2\) solution, at 70°C and pressures ranging from 1 to 6000 kgf/cm\(^2\).

EXPERIMENTAL

Reagents. Chemically pure toluene, p- and m- xylol, and p-chloro and m-bromotoluene were dried over CaCl\(_2\), and then redistilled through a glass-packed column with an efficiency of \(\sim15\) theoretical plates; the p-nitrotoluene was purified by threefold recrystallization from ethanol solution, and then dried over CaCl\(_2\) at \(\sim20^\circ\text{C}\). Each of these compounds was chromatographically pure, its index of refraction, and melting and boiling points agreeing with the values cited in the literature. Purification of the N-BSI and azoisobutyric dinitrile (DAA) was by the methods [4, 6] of. The experimental techniques have been described in [4]. Gas-liquid chromatography (GLC) was used for analyzing the reaction system.

The relative rate constants for H atom detachment by Br were calculated from the reaction product concentrations, using the equation

\[
\frac{k_1}{k_2} = \frac{[\text{R}^1\text{Br}][\text{R}^1\text{H}]}{[\text{R}^2\text{Br}][\text{R}^2\text{H}]}
\]

in which \(k_1\) and \(k_2\) are the respective rate constants for H atom detachment from the hydrocarbons \(\text{R}^1\text{H}\) and \(\text{R}^2\text{H}\). The value of the \([\text{R}^1\text{H}] / [\text{R}^2\text{H}]\) ratio was varied with the amount of N-BSI in the system so as to assure that it would change only insignificantly in the course of the reaction. This method gave precise data on the effect of

TABLE 1. Relative Rate Constants for Detachment of the Benzyl H Atoms of \( RC_6H_4CH_3 \) by \( Br \) Atoms at Various Pressures (N-BSI, 0.03-0.06 mole/liter; DAA initiator, 0.0005-0.005 mole/liter; \( CH_2Cl_2; 70^\circC \); \( R^H \) and \( R^2H \) in twofold excess, or greater, with respect to N-BSI)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>( k_R/kT ) per bond, at various pressures, ( P, \text{kgf/cm}^2 )</th>
<th>Literature data [9]</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Cl</td>
<td>2.24+0.01(5)*</td>
<td>2.56+0.17</td>
</tr>
<tr>
<td>m-Cl</td>
<td>1.34+0.02(4)</td>
<td>1.52+0.05</td>
</tr>
<tr>
<td>H</td>
<td>0.96+0.02(3)</td>
<td>1.22+0.02(3)</td>
</tr>
<tr>
<td>p-Br</td>
<td>1.17+0.01(3)</td>
<td>1.22+0.02(3)</td>
</tr>
<tr>
<td>m-Br</td>
<td>1.66+0.03(3)</td>
<td>1.69+0.03(3)</td>
</tr>
<tr>
<td>p-NO_2</td>
<td>0.91+0.05(3)</td>
<td>0.86+0.05(3)</td>
</tr>
</tbody>
</table>

*The number of experiments is given in parentheses. The attached figures represent values of the mean-square deviation.

Experiment at \( P = 5000 \text{kgf/cm}^2 \).

TABLE 2. Values of the \( \rho \) Constant for Various Pressures

<table>
<thead>
<tr>
<th>( P, \text{kgf/cm}^2 )</th>
<th>( \rho )</th>
<th>( S_0 )</th>
<th>( r )</th>
<th>( \sigma )</th>
<th>( S_1 )</th>
<th>( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.88±0.15</td>
<td>0.118</td>
<td>0.087</td>
<td>-1.71±0.08</td>
<td>0.073</td>
<td>0.995</td>
</tr>
<tr>
<td>2000</td>
<td>-1.63±0.14</td>
<td>0.111</td>
<td>0.085</td>
<td>-1.48±0.08</td>
<td>0.069</td>
<td>0.994</td>
</tr>
<tr>
<td>4000</td>
<td>-1.49±0.14</td>
<td>0.110</td>
<td>0.082</td>
<td>-1.37±0.08</td>
<td>0.070</td>
<td>0.993</td>
</tr>
<tr>
<td>6000</td>
<td>-1.31±0.14</td>
<td>0.112</td>
<td>0.077</td>
<td>-1.20±0.10</td>
<td>0.084</td>
<td>0.987</td>
</tr>
<tr>
<td>80\°C, ( CCl_4 ) [9]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

pressure on relative rate constants, but absolute rate constants obtained with it may have been slightly in error since their calculation involved the use of chromatographic calibration curves for the reaction products. Correction was introduced by calculating relative rate constants at atmospheric pressure (and, in part, at higher pressures as well) through the change in hydrocarbon concentration, using the following equation

\[
\frac{k_1}{k_2} = \frac{\lg [R^H]_{\text{fin}}}{\lg [R^H]_{\text{fin}}}
\]

in which \( k_1 \) and \( k_2 \) are the rate constants and \([R^H]_{\text{fin}}\) and \([R^H]_{\text{fin}}\) the hydrocarbon concentrations measured at the beginning and end of the reaction. Chlorobenzene was used as an internal standard. This combination of methods essentially eliminated the possibility of error from ring bromination [7, 8] which we had detected, in slight degree, in our early work on xylool bromination.

Since the activities of \( p \)-nitrotoluene and toluene were quite different, the former was brominated in a \( m \)-bromotoluene mixture and the rate constant then recalculated to toluene, the standard, a procedure leading to a considerable improvement in the accuracy of analysis.

**DISCUSSION OF RESULTS**

Values of the relative rate constants for benzyl H atom detachment in substituted toluenes, and at various pressure, are shown in Table 1. Values obtained under similar conditions and at \( 1 \text{ kgf/cm}^2 \) pressure [9] are shown in the last column of this table for comparison. The data of Table 1 were used in developing Tables 2-4. Calculation were carried out by least-squares methods, using the BESM-4 computer.

Table 2 shows values of \( \rho \) for the electrophilic substituent constants, \( \sigma \) and \( \sigma^+ \), at various pressures [10].

It is seen from Tables 1 and 2 that our own data at atmospheric pressure are consistent with those reported in [9]. The fact that our atmospheric pressure values of \( \sigma \) are somewhat high may have been due to the fact that our experiments were carried out at lower temperatures. Values of the \( \Delta V^p_R - \Delta V^p_T \) difference calculated with the correlation equation of [11, 12] are shown in Table 3. Here \( \Delta V^p_R \) and \( \Delta V^p_T \) are the respective volume effects attending H atom detachment from the substituted and the unsubstituted toluene. The values of \( S_0 \), the standard deviation, indicate that the precision of calculation fell within the limits of the experimental error in the determination of the relative rate constants.