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EFFECTS OF PRESSURE ON ORGANIC REACTIONS* II

The Acid-Catalyzed Rearrangement of Pinacol

BY TAKASHI MORIYOSHI AND KATSUHIRO TAMURA

The effect of pressures up to 1,447 bar on the rate of the acid-catalyzed rearrangement of pinacol has been measured at 60-70°C in dilute hydrochloric acid and at 25°C in concentrated sulfuric acid. The volumes of activation in the former at 1 bar are in the range from 6.8 to 8.4 cm³/smol, and decrease as the temperature rises. The energy and entropy of activation at 1 bar are 36.1 kcal/mol and 22.3 cal/deg·mol, respectively, and both increase with increasing pressure. On the other hand, the volume of activation in the latter at 1 bar is 6.1 cm³/smol in 47.5 wt% and 5.5 cm³/smol in 55.8 wt% sulfuric acid. A modified mechanism for the rearrangement has been discussed in the light of these results. Consequently, it is suggested that the slow step is the migration of the methyl group of the intermediate ion (R−−OH₂⁺) formed from the protonated pinacol and is not probably varied with the acidity of the solution.

Introduction

The acid-catalyzed rearrangement of pinacol has been thought to proceed according to the A-1 mechanism on the basis of the Zucker-Hammett hypothesis from the evidence that the rate is proportional to the Hammett acidity function h₀. But the explanations about the mechanisms proposed for the rearrangement are not necessarily the same in details. For instance, Duncan et al. and Deno et al. concluded that the reaction proceeded directly from the conjugate acid of pinacol to pinacolone, and it was not through the carbonium ion as an intermediate. On the other hand, Bunton et al. reported from the evidence of O₁₈ exchange experiments on pinacol that solvent water captures ca. 70% of carbonium ions, regenerating the pinacol enriched in O₁₈ at relatively low acidities and in such an acid concentration the slow step should be the conversion of carbonium ion into pinacolone, possibly synchronizing with proton removal. Furthermore, they considered that at higher acidities, such as 50 wt.% sulfuric acid, more than 90% of carbonium ions would be rearranged to pinacolone and the rate of rearrangement becomes similar to that of formation of carbonium ions. The result of 2-methylpropane-1,2-diol as a related reaction is also consistent with the conclusion that the slow step is the...
formation of carbonium ion from the conjugate acid of the glycol.

Recently, Stiles and Mayer\(^6\) has proposed a new mechanism that involves the formation of a "carbonium hydrate" structurally analogous to an "intimate ion pair" and is relatively close to the concerted process in which the elimination of a water molecule from the protonated pinacol is accompanied rather than followed by the migration of the alkyl group.

In many organic reactions it is well-known that the volume of activation helps to reveal the mechanism and gives frequently a useful information about the structural details of the transition state. Thus, in order to examine the mechanism by means of the volume of activation, the effect of pressure on the rate of rearrangement of pinacol has been measured. In addition, an attempt to seek evidence on the question whether the rate-controlling step varies with the acidity of solution has been also made by measuring the volume of activation in concentrated sulfuric acid.

**Experimental**

**Materials**

Pinacol was prepared from acetone\(^7\), and recrystallized from benzene as the hexahydrate, mp. 47°C. The solution of hydrochloric acid used as a catalyst was made by diluting the analytical grade concentrated acid and standardized with sodium carbonate solution. The concentrated solutions of sulfuric acid as a solvent were prepared by the volume method and the exact composition was determined by the density measurement. All other chemicals used were of reagent grade and were not further purified.

**Analytical methods**

The rate of rearrangement in dilute aqueous hydrochloric acid was followed by the conventional periodate titration for unchanged pinacol; 5 ml of the reaction mixture was added to a mixture containing 10 ml of saturated sodium hydrogen carbonate solution and 10 ml of 0.02 mole/l periodic acid, and the resulting solution was allowed to stand for over night at room temperature. Then 10 ml of 2N hydrochloric acid and 10 ml of 1.2 mole/l potassium iodide solution were added, and the iodine liberated was titrated with 0.1N sodium thiosulfate solution using starch as indicator.

On the other hand, for the reaction in concentrated sulfuric acid the rate was determined by measuring the optical density of the reaction mixture with a Hitachi Model-139 spectrophotometer. The measurements were done at 271 m\(\mu\) in 47.5 wt% sulfuric acid and at 267 m\(\mu\) in 55.8 wt%, at which an absorption maximum of pinacolone exists.

**Apparatus and procedure**

The runs at atmospheric pressure were carried out under nitrogen atmosphere in a glass vessel immersed in a thermostat controlled within ± 0.05°C of the setting temperature.

Under high pressure, the apparatus shown in Fig. 1 was used. The reaction mixture was enclosed

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in a glass syringe with a teflon cap, put in the pressure vessel which was filled with silicone oil as pressure-transmitting fluid and placed in the thermostat. The pressure vessel was sealed by "unsupported area" packing of teflon and neoprene rubber rings. The pressure was generated by means of a high-pressure hand pump connected with the apparatus and was measured directly by a Bourdon tube gauge, which was calibrated against a pressure balance made by the American Instrument Co. Inc.

The reaction mixture was prepared by the volume method using acid and pinacol solutions of known concentrations at room temperature, and was quickly poured into the reaction vessel.

Results

The rate was measured usually over a range of 0—50% of complete reaction. Each solution was measured at least twice under a given condition.

Since the reaction was kinetically of first order in pinacol, the first order rate constants $k_{\text{a1}}$ for runs with dilute solution of hydrochloric acid were obtained graphically in usual way. The kinetical results are listed in Table 1. The second order rate constants $k_{\text{a2}}$ given were obtained by dividing the first order constants $k_{\text{a1}}$ by the concentration of acid corrected for the compression and thermal expansion of the reaction mixture, which were assumed to be the same as that of water*

For reactions in concentrated acid, 55.8% sulfuric acid solution, first order rate constants were

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Effects of Pressure on Organic Reactions II

Table 1 Rate constants for the rearrangement of pinacol catalyzed by hydrochloric acid

<table>
<thead>
<tr>
<th>$T, ^{0}C$</th>
<th>$P, \text{bar}$</th>
<th>$[C_{\text{pinacol}}, \text{mole}^{-1}]$</th>
<th>$10^6 k_{a1}, \text{sec}^{-1}$</th>
<th>$10^6 k_{a2}, \text{mole}^{-1}\cdot\text{sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1</td>
<td>0.885</td>
<td>2.58</td>
<td>2.96</td>
</tr>
<tr>
<td></td>
<td>467</td>
<td>0.885</td>
<td>2.12</td>
<td>2.38</td>
</tr>
<tr>
<td></td>
<td>955</td>
<td>0.871</td>
<td>1.87</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>1447</td>
<td>0.885</td>
<td>1.64</td>
<td>1.78</td>
</tr>
<tr>
<td>65</td>
<td>1</td>
<td>0.871</td>
<td>5.65</td>
<td>6.61</td>
</tr>
<tr>
<td></td>
<td>467</td>
<td>0.871</td>
<td>4.90</td>
<td>5.62</td>
</tr>
<tr>
<td></td>
<td>955</td>
<td>0.871</td>
<td>4.45</td>
<td>5.02</td>
</tr>
<tr>
<td></td>
<td>1447</td>
<td>0.871</td>
<td>4.13</td>
<td>4.58</td>
</tr>
<tr>
<td>70</td>
<td>1</td>
<td>0.871</td>
<td>12.4</td>
<td>14.5</td>
</tr>
<tr>
<td></td>
<td>467</td>
<td>0.871</td>
<td>11.0</td>
<td>12.6</td>
</tr>
<tr>
<td></td>
<td>955</td>
<td>0.871</td>
<td>9.97</td>
<td>11.3</td>
</tr>
<tr>
<td></td>
<td>1447</td>
<td>0.871</td>
<td>9.08</td>
<td>10.1</td>
</tr>
</tbody>
</table>

The reaction mixture was initially about 0.03 mole/l in pinacol at room temperature and pressure. The concentration of hydrochloric acid shows the value at room temperature and pressure. Obtained graphically by plotting $\ln(D_m-D_c)$ against time $t$, where $D_m$ and $D_c$ are the optical densities of the reaction mixture after the completion of reaction (practically, 98% of complete reaction) and after time $t$, respectively. In 47.5 wt% solution the rate was fairly slow, so that a long time was required for the estimation of $D_m$. Therefore, in this case the first order rate constants were determined conveniently from the slope of a graph of $\ln(D_{t+\Delta t}-D_c)$ against time $t$ by the application of Guggenheim's method9), where the interval of time $\Delta t$ was about two fold of the half-life. The kinetical

Table 2 Rate constants for the rearrangement of pinacol in concentrated sulfuric acid at 25°C

<table>
<thead>
<tr>
<th>$\text{H}<em>{2}\text{SO}</em>{4}, \text{wt}%$</th>
<th>$P, \text{bar}$</th>
<th>$10^6 k_{a1}, \text{sec}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>47.5 (3.10)</td>
<td>1</td>
<td>9.68</td>
</tr>
<tr>
<td></td>
<td>216</td>
<td>9.15</td>
</tr>
<tr>
<td></td>
<td>467</td>
<td>8.73</td>
</tr>
<tr>
<td></td>
<td>955</td>
<td>7.62</td>
</tr>
<tr>
<td></td>
<td>1,447</td>
<td>6.77</td>
</tr>
<tr>
<td>55.8 (4.00)</td>
<td>1</td>
<td>67.7</td>
</tr>
<tr>
<td></td>
<td>216</td>
<td>65.5</td>
</tr>
<tr>
<td></td>
<td>467</td>
<td>60.7</td>
</tr>
<tr>
<td></td>
<td>955</td>
<td>55.2</td>
</tr>
<tr>
<td></td>
<td>1,447</td>
<td>48.9</td>
</tr>
</tbody>
</table>

Initial concentrations of pinacol at room temperature and pressure were $2.49\times10^{-2}$ mole/l in 47.5 wt% sulfuric acid and $2.19\times10^{-2}$ mole/l in 55.8 wt%. The number in parenthesis denotes the value of $-H$.

9) E. A. Guggenheim, Phil. Mag., 2, 538 (1926)
results in both solutions are listed in Table 2, in which the rate constants are not converted to the second order constants because neither the compressibility nor the pressure dependence on the acidity of concentrated sulfuric acid is available in the literatures and in addition the rate at higher acid concentrations as the present conditions are unlikely of first order in acid.

Fig. 2 Arrhenius plot for the rearrangement of pinacol catalyzed by hydrochloric acid

Table 3 Energies and entropies of activation for the rearrangement of pinacol

<table>
<thead>
<tr>
<th>P, bar</th>
<th>E, kcal-mole⁻¹</th>
<th>ΔS*, cal-deg⁻¹·mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>36.1</td>
<td>22.3</td>
</tr>
<tr>
<td>467</td>
<td>37.0</td>
<td>24.6</td>
</tr>
<tr>
<td>955</td>
<td>37.9</td>
<td>27.0</td>
</tr>
<tr>
<td>1,447</td>
<td>38.7</td>
<td>29.1</td>
</tr>
</tbody>
</table>

An Arrhenius plot for the reaction catalyzed by hydrochloric acid is given in Fig. 2, and shows fairly better straight lines at each pressure. Table 3 shows the values of activation parameters calculated from these plots. The activation energy obtained at 1 bar is in fairly good agreement with the values of 32.7 kcal/mole determined by Duncan et al. and 33.7 kcal/mole by Bunton et al. Also this is comparable to the value 31 kcal/mole estimated for the rearrangement of benzopinacol by an analogous reaction process. The second order rate constants as a function of pressure at each temperature are shown in Fig. 3. Similarly the first order rate constants in concentrated acid are also plotted against pressure in Fig. 4.

All of them were fitted graphically to the equation,

$$\log k = a + bP,$$

and the volume of activation at 1 bar was calculated from those slopes using the equation,

$$\left( \frac{\partial \ln k}{\partial P} \right)_T = -\frac{AV^*}{RT} = 2.303b.$$

The results are summarized in Table 4.

<table>
<thead>
<tr>
<th>$T$, °C</th>
<th>$AV^*$, cm³·mole⁻¹</th>
<th>$T$, °C</th>
<th>$H_2SO_4$, wt %</th>
<th>$AV^*$, cm³·mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>8.4</td>
<td>25</td>
<td>47.5</td>
<td>6.1</td>
</tr>
<tr>
<td>65</td>
<td>7.6</td>
<td>25</td>
<td>55.8</td>
<td>5.6</td>
</tr>
<tr>
<td>70</td>
<td>6.8</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For comparison with values measured by Deno et al. and Stiles et al., the rate constants in sulfuric acid at 25°C and 1 bar were plotted against the Hammett acidity function $H_\alpha$. The values of $H_\alpha$ used were taken by interpolating the data of Long and Paul. The result is given in Fig. 5, in which our values lie on the best straight line through the points and the agreement with acidity dependence

is shown to be satisfactory. The \( p \)-value given by the equation,

\[
\log k_r = -pH + \text{constant},
\]

is found to be 0.95 from the graph.

Fig. 5 Dependence of \(-H_0\) on the rate of the rearrangement of pinacol at 25\(^\circ\)C and 1 bar

- O: Deno et al. 39
- ☀: Stiles et al. 59
- ●: this work

Discussion

Reaction mechanism

The carbenium ion mechanism 12-15, in which the carbenium ion formation is rate-determining and the so-called concerted mechanism 13-14 involving the direct decomposition of the protonated pinacol into pinatolone, has been so far proposed for the rearrangement of pinacol. However, to account for the recent evidences related to the oxygen exchange 13-14 and the migration tendencies of alkyl groups 14 in the rearrangement, both remain somewhat in doubt and are inadequate. So some modifications are possible on the grounds of the consideration by Stiles et al. 59 and the inference from analogy with alcohol dehydration 14. It becomes apparent from the detailed discussion presented later that a possible mechanism for the rearrangement of pinacol in strong acid solution may be envisaged as follows:

\[
P_{\text{OH}} + H_2O^+ \xrightleftharpoons{K_1} \text{POH}_2^+ + H_2O, \quad (i)
\]

\[
\frac{K_2}{k_{-2}} \xrightarrow{K_2} (P--OOH)_2^+, \quad (ii)
\]

13) Y. Pocker, Chem. Ind., 1959, 332
Effects of Pressure on Organic Reactions II

\( (P-\text{-OH})^+ \xrightarrow{k_3} \text{KH}^+ + H_2O, \)  
\( \text{KH}^+ + H_2O \xrightarrow{\text{fast}} K + H_3O^+ \),

where \( \text{POH} \) represents the pinacol, \( K \) the pinacolone and \( (P-\text{-OH})^+ \) an intermediate ion, similar to the "carbocation hydrate" named by Stiles et al.\(^{(a)}\).

If one assumes a steady state concentration of the intermediate ion \( (P-\text{-OH})^+ \), the overall rate of rearrangement can be expressed by the equation,

\[
\text{rate} = \frac{K_r \cdot k_z \cdot k_s \cdot h_v \cdot [\text{POH}]}{k_{-2} + k_3}
\]

where \( k \)'s are the rate constants, \( K_r \) the equilibrium constant for the first step (i), \( h_v \) the Hammett acidity function and the brackets denote the concentration terms.

Assuming the limiting case where \( k_{-2} \gg k_3 \), the rate equation reduces to

\[
\text{rate} = K_1 \cdot K_2 \cdot k_3 \cdot h_v \cdot [\text{POH}]
\]

where \( K_2 \) is the equilibrium constant for the second step (ii). In agreement with observed kinetic results, the rearrangement is found to be first order in pinacol and the rate to be proportional to the Hammett acidity function \( h_v \).

Volumes of activation

The measured volumes of activation are positive, and decrease with increasing temperature, which implies evidently that the initial state is thermally more expansible than the transition state as expected also from the results of the entropy of activation. Further detailed consideration about the volume of activation will be given below.

The apparent second order rate constant \( k_{a2} \) obtained experimentally in dilute aqueous hydrochloric acid is given by the equation,

\[
\text{rate} = k_{a2} [\text{HCl}] [\text{POH}].
\]

By comparison of equations (2) and (3),

\[
k_{a2} = K_1 \cdot K_2 \cdot k_3 \cdot h_v / [\text{HCl}]
\]

Therefore, the measured volume of activation \( \Delta V^* \) is actually represented as a composite quantity as follows:

\[
\Delta V^* = \Delta V_1 + \Delta V_2 + \Delta V_3^* + \frac{RT \partial \ln([\text{HCl}]/h_v)}{\partial P},
\]

where \( \Delta V_1 \) and \( \Delta V_2 \) represent the volume changes for the steps (i) and (ii), respectively, and \( \Delta V_3^* \) the volume of activation for the slow step (iii). The fourth term on the right hand side in equation (5) can be estimated approximately in the following way: if the change of \( h_v \) with pressure could be assumed to be due to only the change of the concentration of acid with pressure, then

\[
\frac{RT \partial \ln([\text{HCl}]/h_v)}{\partial P} = RT \kappa \left[ 1 - \frac{\partial \ln h_v}{\partial \ln [\text{HCl}]} \right],
\]

where \( \kappa \) is the compressibility of the solution.

In \([\text{HCl}] = 0.871 \sim 0.885 \text{ mole/l} \), \( \frac{d \ln h_s}{d \ln [\text{HCl}]} = 1.36 \) from the variation of \( h_s \) with the concentration of hydrochloric acid at 25°C\(^1\). Using the compressibilities of water\(^2\) or aqueous hydrochloric acid taken by interpolating the data from the literature\(^3\),

\[
\frac{RT \ln([\text{HCl}]/h_s)}{dP} \approx 0.40 \sim 0.42 \text{ cm}^3/\text{mole}
\]

Evidently, the variation of \( h_s \) with pressure is small and insignificant in the case of so dilute acid as in this work, and then it follows from the observed values of \( dV^* \) that

\[
\Delta V_1 + \Delta V_2 + \Delta V_3^* \approx 7.2 \sim 8.8 \text{ cm}^3/\text{mole}
\]

in the experimental temperature range.

In the pre-equilibrium proton transfer (i), there is no change in the number of molecules and probably little change in the electrostriction of the solvent, so that the volume change \( \Delta V_1 \) should be slightly positive and not so different from zero\(^4\). Hence, it follows that the measured volume of activation is mainly determined by the sum of \( \Delta V_2 \) and \( \Delta V_3^* \).

In order to elucidate the location of the transition state on the reaction coordinate, we determined the volume change for the complete reaction from the density measurement, and found to be \( 30 \pm 0.5 \text{ cm}^3/\text{mole} \) at 65°C and 1 bar. The partial molar volume of pinacol is less than that of pinacolone by \( 12 \text{ cm}^3/\text{mole} \), and this results from strong hydrophilic character of the hydroxyl group of pinacol. From these results, the volume of activation \( \Delta V^* \) is about one third the volume change of complete reaction \( \Delta V \), and so the transition state can be located closely to the initial state in volume and seems to have the character similar to pinacol. The present mechanism may be also valid on the view of these.

The conversion of a van der Waals bond between a molecule and the conjugate acid of substrate to a partial valence bond in the transition state results in the decrease of volume of about \( 10 \text{ cm}^3/\text{mole} \), as found in most acid-catalyzed hydrolysis\(^5\). On the basis of this evidence, if the intermediate ion \((\text{P}--\text{OH}_2)^* \) is structurally similar to the transition state in which a molecule of water takes part in the A-2 mechanism, then the volume change \( \Delta V_2 \) of step (ii) becomes about \( 8 \text{ cm}^3/\text{mole} \). This value is little different from that of \( \Delta V_1 + \Delta V_2 + \Delta V_3^* \) estimated above. Consequently, the volume of activation for the slow step (iii) seems to be near to zero or slightly negative, which is not hard to understand because there is an intramolecular migration of the methyl group to the \( \alpha-C \) atom without further appreciable elongation of the \( \text{C}--\text{OH}_2 \) bond and there will be more diffusion of the positive charge in the transition state than in the original ion \((\text{P}--\text{OH}_2)^* \).

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The effect of pressure on the rearrangement in concentrated sulfuric acid could be also discussed in the same manner. Since the apparent first order rate constant obtained is expressed by

\[ k_{a1} = \frac{K_1 \cdot K_2 \cdot k_1 \cdot k_2}{h_0} \]  

the volume of activation is given by

\[ \Delta V^* = \Delta V_1 + \Delta V_2 + \Delta V_3^* - \frac{RT \partial \ln h_0}{\partial P} \]  

Since the variation of \( h_0 \) with the concentration of acid at 25°C is

\[ \frac{d \ln h_0}{d \ln [\text{H}_{2}\text{SO}_4]} = 8.5 \]  

\[ \frac{d \ln h_0}{d \ln [\text{H}_{2}\text{SO}_4]} = 10.3 \]  

by using the compressibility data of Gibson, the dependences of \( h_0 \) on pressure are found to be

\[ \frac{RT \partial \ln h_0}{\partial P} = 6.2 \text{ cm}^3/\text{mole} \]  

\[ \frac{RT \partial \ln h_0}{\partial P} = 7.1 \text{ cm}^3/\text{mole} \]

respectively. Hence, the value of \( \Delta V_1 + \Delta V_2 + \Delta V_3^* \) becomes actually 12.3 cm\(^3\)/mole in the former and 12.7 cm\(^3\)/mole in the latter, and is likely to be little different in these acid concentrations. According to the foregoing discussion, these values may be regarded as being close to \( \Delta V_2 \) itself that arises mainly from the elongation of a covalent bond C-OH\(^+\). For comparison, the value of \( \Delta V_1 + \Delta V_2 + \Delta V_3^* \) at 25°C obtained by extrapolating the results in dilute hydrochloric acid is 14.4 cm\(^3\)/mole compared with that obtained in concentrated acid. The agreement between this value and the corresponding values in concentrated acid is satisfactory, and the small difference is probably due to special properties of the solvent systems. Thus, it may be certainly expected from these evidences that no change of mechanism has essentially occurred with the acidity of solution.

**Energies and entropies of activation**

The activation process in the rearrangement seems to closely resemble that in the dehydration of alcohol to olefin. Boyd et al. have recently proposed a new mechanism proceeding through an encumbered carbonium ion intermediate to the transition state as follows:

They estimated the enthalpies and entropies of activation for alcohol dehydration, that is, \( \Delta H^* = 33.9 \pm 0.3 \text{ kcal/mole} \) and \( \Delta S^* = 19 \pm 2 \text{ cal/deg-mole} \) for t-butyl alcohol, and \( \Delta H^* = 29.1 \pm 0.5 \text{ kcal/mole} \) and \( \Delta S^* = 12 \pm 2 \text{ cal/deg-mole} \) for t-amyl alcohol, respectively. From the thermodynamic and activation parameters for the hydration of dissolved isobutene\(^{20}\) are also derived the values of \( 32.7 \pm 0.2 \text{ kcal/mole} \) and \( 13.3 \pm 0.7 \text{ cal/deg-mole} \) for the corresponding values for dehydration of t-butyl alcohol. Comparing these values with the present results for the rearrangement of pinacol, the enthalpies of activation for both reactions are found to be nearly the same, but the entropies to be less than that of the rearrangement by about 10 cal/deg-mole. This appears to be probably due to the substantial difference between the change of entropy accompanied by the migration of the methyl group in the activation process and that by formation of "\( \pi \)-complex" in the dehydration.

On the basis of these considerations, it is supposed that the mechanism for the rearrangement of pinacol does not essentially differ from that for the dehydration and further the oxygen exchange of alcohol. Accordingly, the intermediate ion \((P-\cdots \text{OH}_2)^+\) presented in the proposed mechanism seems to be almost analogous to the encumbered carbonium ion\(^{140}\) in character.

Although any definitive evidence that a modified carbonium ion is favored over the classical one has not been obtained in this work, it may be concluded from the above discussions that the rearrangement mechanism involving such a reaction intermediate is reasonable in the light of the present results. The character of the intermediate should be argued in more detail with further extensive data.

The authors would like to express their thanks to Professor J. Osugi of Kyoto University for his advice and encouragement.

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