pex is relatively more rigid as compared to ([I-
2-isopropanol]) complex. The activation energy \( E_a \) in the isopropanol reaction is lower than the cor-
responding acetone reaction and the rate constants \( k \) also show the same trend. However, the transition
complex has a much lower \( \Delta S^\circ \) value in the case of isopropanol than in the case of acetone reaction.

The authors are thankful to Prof. T. Navaneeth Rao and Dr B. Sethuram for helpful suggestions
and to Prof. M. M. Taqui Khan for necessary facil-

References

   11 (1973), 246.
   Soc., 50 (1973), 211.
3. SAIPRAKASH, P. K., SETHURAM, B. & NAVANEETH RAO,
4. SINGH, A. K., KATVALL, MOHAM & SINGH, R. P., Indian
5. MUHAMMAD, S. S. & SETHURAM, B., Acta chim. hung.,
   46 (1965), 115, 125.
   3276.
   14A (1976), 45.
8. FERRE, E., Spot tests in organic analysis (Elsevier, New
9. SAIPRAKASH, P. K., A kinetic study of some aspects of
   oxidation of organic substances by peroxides, Ph.D. thesis,
   OSmania University, 1974, 70, 77.
10. SINGH, R. N. & SINGH, H. S., Indian J. Chem., 14A
    (1978), 139.

Kinetics of Oxidation of Aniline & ortho- &
meta-Toluidines by N-Chlorobenzamide

B. S. RAWAT & M. C. AGRAWAL*
Department of Chemistry, Harcourt Butler Technological
Institute, Kanpur 208002

Received 26 June 1978; accepted 25 September 1978

The kinetics of oxidation of aniline, o- and m-tolui-
dines by N-chlorobenzamide (NCB) have been studied
in acid medium. First order dependence in NCB, H+
and Cl\(^-\) are observed. Azobenzene and substituted
azobenzenes have been obtained as the main oxidation
products. The influence of ionic strength is negligible.
The activation energies are in the range 18.4 to 20.7
kcal/mol. A mechanism for the oxidation process is
proposed.

OXIDATION kinetics of semicarbazide and ascorbic acid in acid media by N-chlorobenzamide (NCB) have been reported from our laboratories.

In the present investigation, kinetics of oxidation of aniline, ortho- and meta-toluidines by NCB have been reported and an effort has been made to suggest a possible mechanism of oxidation.

Standard solution of NCB was prepared in methanol. Aniline, ortho- and meta-toluidines were distilled under reduced pressure using a trace of zinc dust during distillation. The amines were then converted into their respective hydrochlorides, washed, dried and recrystallized and their purity

checked by melting points. All the reagents used were of AR, BDH grade. Doubly distilled water was used throughout the course of investigation.

Azobenzene and its substituted derivatives were separated and identified as the main oxidation products, which were confirmed by TLC method as reported by Pauscher et al.\(^3\)

The progress of reaction was followed by estimating NCB iodometrically at different time intervals at several initial concentrations of the reactants (Table 1). The reaction followed first order dependence with respect to [NCB]. An increase in [substrate] from 1.2 to 4.0 \( \times 10^{-3}\) M, had no effect on first order rate constants \( k_1 \) indicating that the order is zero with respect to aromatic amines.

The effects of [H\(^+\)] and [Cl\(^-\)] concentrations were investigated separately at constant ionic strength (Tables 2 and 3). From the slopes of linear log-log plots order in each was found to be

| Table 1 — Effect of Varying Reactant Concentration |
| [MeOH] = 20%; [HCl] = 0.2M |

<table>
<thead>
<tr>
<th>NCB ( \times 10^{-3})</th>
<th>Substrate ( \times 10^{-3})</th>
<th>*( k_1 \times 10^{12} ) sec(^{-1}) at 40°</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>20</td>
<td>10.2 (16.0) 10.0 (14.9) 9.6 (15.0)</td>
</tr>
<tr>
<td>16</td>
<td>20</td>
<td>10.2 (17.1) 9.5 (15.7) 9.8 (15.4)</td>
</tr>
<tr>
<td>20</td>
<td>20</td>
<td>10.1 (16.1) 10.5 (15.5) 9.9 (15.7)</td>
</tr>
<tr>
<td>28</td>
<td>20</td>
<td>10.3 (16.3) 9.8 (15.5) 9.8 (16.1)</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>10.1 (16.0) 9.6 (16.1) 9.7 (16.3)</td>
</tr>
<tr>
<td>20</td>
<td>12</td>
<td>10.1 (14.5) 9.8 (15.4) 9.8 (14.8)</td>
</tr>
<tr>
<td>20</td>
<td>16</td>
<td>10.4 (16.0) 10.0 (15.4) 9.9 (15.4)</td>
</tr>
<tr>
<td>20</td>
<td>40</td>
<td>11.5 (18.5) — — 10.3 (17.0)</td>
</tr>
</tbody>
</table>

*Values of \( k_1 \) in parentheses were obtained at 45°.

| Table 2 — Effect of Varying [H\(^+\)] at Constant Ionic Strength |
| [{NCB} = 2 \( \times 10^{-3}\) M; [Substrate] = 2 \( \times 10^{-3}\) M; MoOH = 20%; Ionic strength = 0.32 M (NaCl)] |

<table>
<thead>
<tr>
<th>[H(^+)] ( \times 10^{-2})</th>
<th>Aniline ( \times 10^{12}) sec(^{-1}) (at 40°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7.7 (13.9) 7.3 (11.9) 7.3 (11.6)</td>
</tr>
<tr>
<td>15</td>
<td>10.9 (18.4) 10.6 (17.5) 10.7 (17.2)</td>
</tr>
<tr>
<td>20</td>
<td>13.8 (23.8) 13.6 (23.3) 14.0 (23.9)</td>
</tr>
<tr>
<td>25</td>
<td>16.8 (26.9) 16.3 (29.5) 16.9 (28.0)</td>
</tr>
<tr>
<td>30</td>
<td>20.4 (31.1) 20.2 (32.6) 20.3 (33.3)</td>
</tr>
</tbody>
</table>

*Values of \( k_1 \) in parentheses were obtained at 45°.

| Table 3 — Effect of Varying [Cl\(^-\)] at Constant Ionic Strength |
| [{NCB} = 2 \( \times 10^{-3}\) M; [Substrate] = 2 \( \times 10^{-3}\) M; [H\(^+\)] = 0.2 M; \( \mu = 0.62\) M (NaClO\(_3\)) |

<table>
<thead>
<tr>
<th>[Cl(^-)] ( \times 10^{-2})</th>
<th>*( k_1 \times 10^{12} ) sec(^{-1}) at 40°</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>13.5 (21.6) 13.0 (23.3) 14.1 (22.4)</td>
</tr>
<tr>
<td>38</td>
<td>16.1 (25.1) 15.9 (26.2) 16.8 (26.2)</td>
</tr>
<tr>
<td>42</td>
<td>17.0 (27.0) 17.8 (29.2) 18.5 (29.4)</td>
</tr>
<tr>
<td>50</td>
<td>21.0 (31.3) 19.6 (33.6) 22.4 (32.6)</td>
</tr>
<tr>
<td>62</td>
<td>24.5 (36.6) 24.9 (40.6) 26.1 (40.6)</td>
</tr>
</tbody>
</table>

*Values of \( k_1 \) in parentheses were obtained at 45°.
approximately unity. Thus the order in HCl was computed as ~2 within permissible limit of error.

The influence of added neutral salts, viz. NaClO₄ was negligible. A variation in NaClO₄ concentration from 0.2 to 1.0 M changed the rate constants from 10⁻¹ to 11.1, 10⁻⁵ to 10⁻⁷, and 9.9 to 10⁻⁴ x 10⁻⁵ sec⁻¹ for aniline, ortho- and meta-toluidines respectively.

The effect of temperature was also studied and the rate constants (k₄) were recorded as 6.0, 10.8, 16.2, 29.7, 46.4 x 10⁻⁵ sec⁻¹ for aniline, 6.5, 10.5, 15.8, 27.0, 40.6 x 10⁻⁶ sec⁻¹ for o-toluidine and 6.0, 9.9, 15.7, 25.8, 40.4 x 10⁻⁶ sec⁻¹ for m-toluidine, at 35°, 40°, 45°, 50° and 55° respectively. The energy of activation was found to be 20.7, 18.4 and 15.8, 19.3, 27.0, 40.6 kcal/mol for aniline, o-toluidine and m-toluidine respectively.

Oxidation of aromatic amines by some oxidizing agents such as lead tetra acetate, peracetic acid, hypochlorous acid, etc. and chlorination by chloramine-T and N-chlorosuccinimide have been reported.

General, except hypochlorous acid oxidation, the slow process of the reaction involves aromatic amine-Tv and N-chlorosuccinimide. In the reaction of aniline, ortho- and meta-toluidines respectively.

Activation of aromatic amines by some oxidizing agents such as lead tetra acetate, peracetic acid, hypochlorous acid, etc. and chlorination by chloramine-T and N-chlorosuccinimide have been reported. In general, except hypochlorous acid oxidation, the slow process of the reaction involves aromatic amine-Tv and N-chlorosuccinimide. In the reaction of aniline, ortho- and meta-toluidines by NCB which follow exactly the same pattern as has been found experimentally. However, due to low solubility of benzamide in water, higher concentrations of benzamide could not be used.

The authors thank Dr S. D. Shukla for encouragement and facilities.

References


Kinetics & Mechanism of the Oxidation of Glycollic, Lactic & α-Hydroxybutyric Acids by Pyridinium Chlorochromate (Corey's Reagent)

KALYAN K. BAKERJ
Department of Chemistry, University of Jodhpur
Jodhpur 342001

Received 12 April 1978 revised and accepted 11 September 1978

The oxidation of glycollic, lactic and α-hydroxybutyric acids by pyridinium chlorochromate yield the corresponding aldo- or keto-acid as the main product. The reaction rates are first order each in the reactants. The reaction is catalysed by acid and the catalysed reaction is nearly first order in acidity. The oxidation of α,a-dideuteroglycollic acid exhibits a kinetic isotope effect (kH/kD) of 5·6±0·05 at 303 K. The reaction rate increases with the introduction of an alkyl group in the organic substrate.