Kinetics and mechanism of the oxidative regeneration of carbonyl compounds from phenylhydrazones by tetramminecopper(2+) bis (permanganate)

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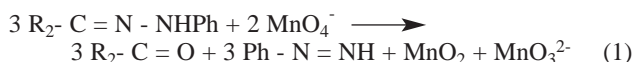
The oxidation of aldo- and keto-phenylhydrazones by tetraamminecopper(2+) bis(permanganate) (TACP), in aqueous acetic acid, proceeds through a mechanism involving the formation of a cyclic activated complex, in the rate-determining step.

Keywords: Oxidative regeneration, hydrazones, tetramminecopper (2+) bis(permanganate), kinetics, mechanism

Tetraamminecopper(2+) bis(permanganate) (TACP) has been reported as a useful oxidizing reagent[2] in 1890. More recently, Seferiadis *et al*[3] have shown, by X-ray crystallography, that it has a distorted octahedral structure with both the permanganate ions being in the coordination shell of copper (II). There seems to be no report about the kinetics and mechanism of oxidative regeneration from hydrazones by TACP. We report here the kinetics of the oxidative regeneration of several aldehydes and ketones from their phenylhydrazones by TACP in aqueous acetic acid solution.

Phenylhydrazones and TACP[4] were prepared by the reported methods. The reactions were studied under pseudo-first-order conditions by keeping a large excess (10 or greater) of the phenylhydrazone over TACP. The solvent was 1:1 (v/v) acetic acid water, unless mentioned otherwise. The reactions were followed by monitoring the decrease in the concentration of TACP at 529 nm spectrophotometrically. The pseudo-first-order rate constant, k_{obs} was evaluated from the linear least-squares plots of log [TACP] *versus* time. We have used coefficient of determination (R^2 or r^2), standard deviation (sd) and Exner's[6] parameter, ψ, as the measures of goodness of fit in correlation analysis.

The oxidation of the phenylhydrazones resulted in the formation of corresponding carbonyl compounds. The oxidation state of manganese in a completely reduced reaction mixture, as determined by an iodometric method, is 3.90 ± 0.14. The analysis of products indicated the following overall reaction.

$$3 R_2\text{-}C = N\text{ - }NHPh + 2 MnO_4^- \longrightarrow$$
$$3 R_2\text{-}C = O + 3 Ph\text{ - }N = NH + MnO_2 + MnO_3^{2-} \quad (1)$$

Thc oxidation of acetaldophenylhydrazone by TACP, in an atmosphcre of nitrogen failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation. This indicated that a one-electron oxidation, giving rise to free readicals, is unlikely.

The reaction is first order with respect to both TACP and thc hydrazone. The rate constants were determined at different temperatures and the activation parameters were calculated.

When successive scans of oxidation of acetophenylhydrazone (0.003 mol dm^{-3})by TACP (0.0004 mol dm^{-3}), in the UV-VIS region, were obtained on a HP Diode-Array rapid scanning spectrophotometer (Model 8452A), a series of curves were obtained. An excellent isosbestic point is obtained when the reaction is monitored by absorption spectroscopy. Thus the reaction is simple from spectrophotometric point of view. This suggests that the reaction does not involve a complicated sequence of events.

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Table 3   Reaction constants for the oxidation of phenylhydrazone of aliphatic aldehydes and ketones by TACP[a]

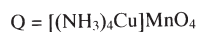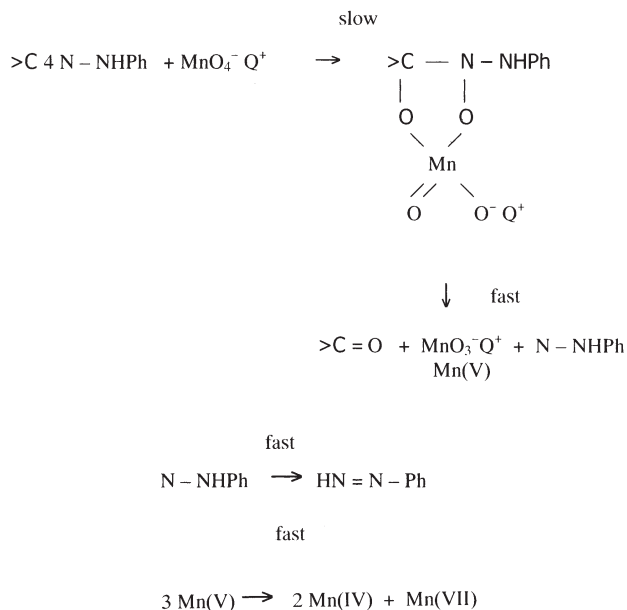| Temp./K	ρ^*	δ	R^2	sd	ψ
288	0.26 ± 0.01	1.05 ± 0.01	0.9997	0.02	0.02
298	0.24 ± 0.01	1.02 ± 0.01	0.9996	0.02	0.02
308	0.22 ± 0.01	1.00 ± 0.01	0.9999	0.01	0.01
318	0.19 ± 0.01	0.98 ± 0.01	0.9998	0.01	0.02

[a] No. of compounds = 9

We could not find any report about the mechanism of the reaction between a hydrazone and a permanganate derivative. However, the reaction of alkenes with permanganate ion has been well studied[10]. The rate of oxidation of ketophenylhydrazones is much less as compared to that of the aldophenylhydrazones. The reason for the slower reaction of ketophenylhydrazones must be steric. As the central carbon changes from a trigonal to a tetragonal state, the crowding around it increases. This increase in the steric crowding will be more in the case of ketophenylhydrazones as compared to that in aldophenylhydrazones. This observation is supported by the correlation analysis of the reactivity of the aliphatic phenylhydrazones also. The rate of oxidation of the aliphatic phenylhydrazones did not yield significant correlation separately with Taft's σ^* and Es values. The rates were, therefore, correlated with Pavelich-Taft's[12] dual substituent-parameter equation (4).

$$\log k_2 = \rho^* \Sigma\sigma^* + \delta\Sigma E_s + \log k_0 \quad (4)$$

The rates exhibited excellent correlations in terms of the Pavelich-Taft equation (Table 3); the reaction constants are being positive.

The observed low positive polar reaction constant points to a cyclic transition state in which the formation of the bond between parmanganate-oxygen and the carbon is somewhat ahead of the formation of the N–O bond. This supports a nucleophilic attack by a permanganate-oxygen on the carbon. The positive steric reaction constant points to a steric hindrance by the substituents. Therefore, the following mechanism (Scheme 1) is proposed for the reaction. The mechanism is supported by the values of activation parameters also. The low values of enthalpy of activation indicate that the bond-cleavage and bond-formation are almost synchronous. The large negative entropies of activation support the formation of a rigid cyclic activated complex from two acyclic molecules.

$$>C\ 4\ N-NHPh\ +MnO_4^-\ Q^+ \quad \xrightarrow{\text{slow}} \quad >C \underset{\substack{| \\ O}}{\overset{}{}} \!\!\!\! N-NHPh$$

Scheme 1 (reaction mechanism):

slow

$$>C\ 4\ N-NHPh\ +\ MnO_4^-\ Q^+ \rightarrow\ >C\underset{O}{|}\!\!-\!\!\underset{O}{|}N-NHPh$$

with Mn bridged:

$$O \diagdown \diagup$$
$$Mn$$
$$O \diagup\!\!\diagup \quad \diagdown\ O^-\ Q^+$$

↓ fast

$$>C=O\ +\ MnO_3^-Q^+\ +\ N-NHPh$$
$$Mn(V)$$

fast

$$N-NHPh \xrightarrow{} HN=N-Ph$$

fast

$$3\ Mn(V) \xrightarrow{} 2\ Mn(IV)\ +\ Mn(VII)$$

$$Q = [(NH_3)_4Cu]MnO_4$$

Scheme 1

Techniques used: Absorption spectrometry; Chromatography; Correlation Analysis

Table 1. Rate constants for the oxidation of acetaldophenylhydrazone by TACP at 288K.

Table 2. Rate constants and activation parameters of the oxidation of phenylhydrazones ($R^1\ R^2\ C = N$-NHPh) by TACP.

Figure 1. Successive scans for the oxidation of acetaldophenylhydrazone (0.003 mol dm^{-3}) by TACP (0.0002 mol dm^{-3}) in 1:1 acetic acid-water at 30863 K (isosbestic point at 475 nm).

References: 19

Figures:1

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