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# Kinetics of Oxidation of Cyclic Alcohols by Quinolinium Dichromate

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When treated with quinolinium dichromate (QDC) in acid medium using dimethylformamide as the solvent, cyclic alcohols were converted to the corresponding cyclic ketones. Kinetic data have been presented. The order of reactivity was $8>7>5>6$. The reaction proceeds via a cyclic transition state, with the subsequent cleavage of the carbon–hydrogen bond ($k_H/k_D=5.8$) in the rate determining step. The electrocyclic mechanism involved six electrons, and being a Hückel-type system ($4n+2$), this was an allowed process.

Cyclic alcohols have been converted to the corresponding cyclic ketones in good yields, using diverse oxidants such as dipyridine–$Cr^{VI}$oxide in dichloromethane,[1] pyridinium chlorochromate in dichloromethane,[2] poly[vinyl(pyridinium chlorochromate)],[3] pyridinium dichromate in dichloromethane,[4] pyridinium fluorochromate in dichloromethane,[5] halosilanes/$CrO_3$,[6] chromium peroxide complexes,[7] 3-carboxypyridinium dichromate,[8] pyridinium chlorochromate in chloroform,[9] hydrogen peroxide catalyzed by methyltrioctylammonium tetrakis(oxodiperoxotungsto)phosphate (3−),[10] acetone in the presence of ruthenium complexes,[11] *t*-butylhydroperoxide in the presence of catalytic amounts of ruthenium trichloride,[12] trichloromelamine in dichloromethane,[13] manganese dioxide catalyzed by ruthenium using a quinone as hydrogen transfer mediator,[14] and by quinolinium fluorochromate in dichloromethane.[15] In continuation of our work on the kinetics of oxidation of organic substrates by quinolinium dichromate (QDC),[16] the present work highlights the kinetic aspects of the oxidation of secondary alcohols by QDC. Selective oxidation of hydroxyl functions plays a pivotal role in organic synthesis. We were prompted to explore the potential of QDC for alcohol oxidation. Our purpose was two-fold: (a) this study allowed us to broaden the scope of the procedure for the oxidation of secondary alcohols; (b) it led us to find that secondary alcohols could be satisfactorily oxidized to ketones by QDC. As a result of this investigation, we could develop an efficient and versatile method for the oxidation of both primary and secondary hydroxyl groups (the oxidation of primary alcohols by QDC has already been reported by us.[17]

## Experimental

**(a) Materials.** All the cyclic alcohols were obtained from the Aldrich Chemical Co., and were purified by distillation, and their purity was checked from physical constants. Quinolinium dichromate (QDC) was prepared by the reported method,[18] and its purity was checked by estimating Cr(VI) iodometrically. Dimethylformamide (DMF) was a BDH sample and was distilled under reduced pressure before use. Sulfuric acid (E. Merck) was used as such after a check of its physical constants. 1-Deuteriocyclohexanol was prepared by the method reported earlier,[19] and its purity was checked by $^1$H NMR spectroscopy.

**(b) Kinetic Measurements.** The reactions were performed under pseudo-first-order conditions, maintaining a large excess of the cyclic alcohols with respect to QDC. The reactions were carried out at constant temperature (±0.1 K) and were followed by monitoring the absorption band at 440 nm, spectrophotometrically, as described earlier.[17] All the reactions were performed under a nitrogen atmosphere. The rate constants were evaluated from the linear ($r$>0.994) plots of log [QDC] against time. The values reported were the mean of two or more runs and were reproducible to within ±3%. The solvent was DMF or DMF–water mixtures. The reaction mixture remained homogeneous in the solvent systems used.

**(c) Product Analysis.** Using the same experimental conditions as were used for kinetic determinations, a solution of the reaction mixture was kept under nitrogen for 24 h, until the reaction had gone to completion. The solution was extracted with ether, the organic layer washed with water, dried over anhydrous $Na_2SO_4$, and then concentrated. The products obtained were the corresponding cyclic ketones (yields: 85—95%), whose boiling points agreed with those reported in the literature. IR analysis exhibited carbonyl bands at 1750 cm$^{-1}$ (cyclopentanone), 1710 cm$^{-1}$ (cyclohexanone), 1700 cm$^{-1}$ (cycloheptanone), and 1690 cm$^{-1}$ (cyclooctanone). The 2,4-dinitrophenylhydrazone (DNP) of the corresponding cyclic ketone was prepared, recrystallized from ethanol, dried and weighed. The product, in each case, was identical (mp) with an authentic sample of DNP of the cyclic ketone. The yields of DNP after recrystallization, with all the cyclic alcohols, were 85—95%.

## Results

The oxidation of cyclic alcohols by QDC in dimethylformamide (DMF) had resulted in the formation of the corresponding cyclic ketone. Under the present experimental conditions, there was no further oxidation of the ketone.

**Stoichiometry.** Stoichiometric experiments were carried out under nitrogen at 323 K as reported earlier.[16] Stoichiometric ratios, Δ[QDC]/Δ[Substrate], in the range 0.65—0.70 were obtained (Table 1), which conformed to the overall equation:

Table 1. Stoichiometry of the Oxidation of Substrates (0.005 M) by QDC[a)]

| | $[H_2SO_4]/M$ | | |
|---|---|---|---|
| Parameter | 0.01 | 0.25 | 0.50 |
| $10^2$[QDC]/M | 2.50 | 2.60 | 2.70 |
| Δ[QDC]/Δ[Cyclopentanol] | 0.65 | 0.68 | 0.71 |
| Δ[QDC]/Δ[Cyclohexanol] | 0.62 | 0.66 | 0.68 |
| Δ[QDC]/Δ[Cycloheptanol] | 0.73 | 0.70 | 0.67 |
| Δ[QDC]/Δ[Cyclooctanol] | 0.69 | 0.72 | 0.67 |

a) $M=mol\,dm^{-3}$.

$$3R_2CHOH + 2Cr^{VI} \longrightarrow 3R_2CO + 2Cr^{III} + 6H^+ \qquad (1)$$

**Kinetic Data.** Under pseudo-first-order conditions, the reactions exhibited first-order dependence on the concentrations of each — substrate and oxidant (Table 2). The reactions were catalyzed by acid, and the catalyzed reaction showed a first-order dependence on acidity (Table 3). These data suggest the following rate law:

$$-d[QDC]/dt = k[\text{Substrate}][QDC][H^+] \qquad (2)$$

**Effect of Solvent.** The acid-catalyzed oxidation of the substrates was studied in solutions containing varying proportions of DMF and water. An increase in the dielectric constant of the medium reduced the rate of the reaction (Table 4).

**Effect of Temperature.** The catalyzed oxidation of the substrates was studied at different temperatures (Table 5), and the activation parameters were evaluated by the standard procedure.[20)]

**Kinetic Isotope Effect.** The rate of oxidation of 1-deuteriocyclohexanol and cyclohexanol at 323 K were $10^4 k_1$ $(s^{-1})$=0.38 and 2.2, respectively. The kinetic isotope effect, $k_H/k_D$, was 5.8 at 323 K.

**Induced Polymerization.** It was observed that there was no induced polymerization of acrylonitrile or the reduction of mercury (II) chloride.[21)] This indicated that a one-electron oxidation was quite unlikely. Control experiments performed in the absence of the substrates did not show any appreciable change in the concentration of QDC.

Table 2. Rate Data for Oxidation of Substrates ($[H_2SO_4]$=0.15 M; $T$=323 K)

| $10^2$[Substrate]/M | 1.0 | 5.0 | 10.0 | 20.0 | 1.0 | 1.0 | 1.0 |
|---|---|---|---|---|---|---|---|
| $10^3$[QDC]/M | 1.0 | 1.0 | 1.0 | 1.0 | 0.5 | 0.25 | 0.10 |
| $10^4 k_1/s^{-1}$ for | | | | | | | |
| Cyclopentanol | 4.1 | 20.2 | 40.8 | 83.0 | 4.2 | 4.0 | 4.3 |
| Cyclohexanol | 2.2 | 11.0 | 22.4 | 44.1 | 2.2 | 2.3 | 2.2 |
| Cycloheptanol | 7.9 | 39.8 | 79.5 | 159 | 7.6 | 7.4 | 7.9 |
| Cyclooctanol | 10.3 | 51.3 | 104 | 206 | 10.1 | 10.6 | 10.2 |

Table 3. Dependence of Rate Constant on Acidity ([Substrate]=0.01 M; [QDC]=0.001 M; $T$=323 K)

| $H_2SO_4/M$ | 0.05 | 0.10 | 0.15 | 0.20 | 0.25 | 0.50 |
|---|---|---|---|---|---|---|
| $10^4 k_1/s^{-1}$ for | | | | | | |
| Cyclopentanol | 1.4 | 2.8 | 4.1 | 5.6 | 7.0 | 14.1 |
| Cyclohexanol | 0.74 | 1.5 | 2.2 | 3.0 | 3.7 | 7.4 |
| Cycloheptanol | 2.6 | 5.3 | 7.9 | 10.4 | 13.1 | 26.0 |
| Cyclooctanol | 3.4 | 6.7 | 10.3 | 13.6 | 17.2 | 34.0 |

Table 4. Dependence of Rate Constant on Solvent Composition ([Substrate]=0.01 M; [QDC]=0.001 M; $[H_2SO_4]$= 0.15 M; $T$=323 K)

| DMF : $H_2O$ (%, v/v) | 100 : 0 | 95 : 5 | 90 : 10 | 85 : 15 | 80 : 20 |
|---|---|---|---|---|---|
| $D$ | 37.6 | 39.7 | 41.8 | 43.9 | 46.1 |
| $10^4 k_1/s^{-1}$ for | | | | | |
| Cyclopentanol | 4.1 | 3.0 | 2.24 | 1.70 | 1.31 |
| Cyclohexanol | 2.2 | 1.62 | 1.24 | 0.98 | 0.77 |
| Cycloheptanol | 7.9 | 5.25 | 3.66 | 2.49 | 1.82 |
| Cyclooctanol | 10.3 | 6.46 | 4.35 | 3.0 | 2.09 |

Table 5. Dependence of Rate Constant on Temperature and Activation Parameters ([Substrate]=0.01 M; [QDC]= 0.001 M; $[H_2SO_4]$=0.15 M)

| Temperature (± 0.1 K) | Cyclo-pentanol | Cyclo-hexanol | Cyclo-heptanol | Cyclo-pctampl |
|---|---|---|---|---|
| | $(10^4 k_1/s^{-1})$ | | | |
| 313 | 2.75 | 1.38 | 5.50 | 7.24 |
| 318 | 3.39 | 1.74 | 6.61 | 8.51 |
| 323 | 4.10 | 2.20 | 7.90 | 10.3 |
| 328 | 5.01 | 2.69 | 9.55 | 12.0 |
| 333 | 6.17 | 3.31 | 11.2 | 14.1 |
| $\Delta H^{\neq}$ $(kJ\,mol^{-1})$ | 33 | 36 | 29 | 26 |
| $\Delta S^{\neq}$ $(JK^{-1}mol^{-1})$ | −209 | −205 | −216 | −222 |
| $\Delta G^{\neq}$ $(kJ\,mol^{-1})$ | 100 | 102 | 99 | 98 |
| Error limits | $\Delta H^{\neq}$ ±2 $kJ\,mol^{-1}$<br>$\Delta G^{\neq}$ ±2 $kJ\,mol^{-1}$ | | $\Delta S^{\neq}$ ±4 $JK^{-1}mol^{-1}$ | |

## Discussion

An examination of the kinetic data obtained, in the present investigation, showed that the rate of oxidation of cyclic alcohols was dependent on the first powers of the concentrations of each — substrate, oxidant, and acid (Tables 2 and 3). The acid catalysis of the reaction must be related to the structure of the oxidant (QDC) which was converted to a protonated species. Earlier reports have established the involvement of protonated Cr(VI) species in chromic acid oxidations.[22,23)]

The dielectric constants for dimethylformamide—water mixtures were estimated from the dielectric constants of the pure solvents (Table 4). Plots of log $k_1$ against the inverse of the dielectric constants were linear ($r$=0.994) with positive slopes, suggesting an interaction between a positive ion and a dipole.[24)]

Reaction rates for cyclic compounds have been rationalized by the difference in strain energy between the ground state and the transition state of the molecule in the process considered.[25)] The rates of oxidation of secondary alcohols with chromic acid have been interpreted with a decrease or increase of steric strain during the conversion of the $sp^3$ hybridized alcohol to the $sp^2$ hybridized ketone.[22,26)] In cyclic systems, changes in bond hybridization produced concomitant changes in various kinds of strains — angle, torsional and transannular.[27)] In the present study, the order of reactivity for the oxidation of cyclic alcohols by QDC was $8>7>5>6$. This order of reactivity could be rationalized on the basis of a change in ring strain involved on passing from the initial ($sp^3$) to the transition state ($sp^2$). In the 5-, 7-, and 8-membered ring systems, the primary source of strain arises as a result of non-bonded interactions. Such interactions would be absent in the ground state of the 6-membered ring system (staggered form). The net result would be that reactions leading to the easing of some of these non-bonded interactions in 5-, 7-, and 8-membered ring systems would be facilitated. Earlier work has shown that the non-bonded interactions of the alcohols are mostly, if not entirely, relieved.[28)] The structure of the transition state must be such that this strain relief could occur, enabling the postulation of a product-like transition state. On the contrary, for the 6-membered ring system, any deviation from the staggered conformation would be unfavorable since this would entail a higher energy of activation. This would account for the slowness in the rate of oxidation of cyclohexanol.

Oxidations of primary and secondary alcohols by Cr(VI) had involved esterification and base-catalyzed, or cyclic, decomposition of the ester by the slow rupture of the carbon–hydrogen bond.[29)] The oxidation of cyclohexanol by $Ce^{IV}$[30)] and $Co^{III}$[31)] had yielded values of $k_H/k_D$=1.9 and 1.7 respectively, and had established an acyclic mechanism with a rate-determining C–H bond cleavage. Calculations have shown that the primary kinetic isotope effect depends on the geometry of the transition state and exhibits low values of $k_H/k_D$ (in the range 1—2) for non-linear configurations.[32)] The bromine oxidation of cyclohexanol, with $k_H/k_D=2.9$, is a possible example of a six-membered transition state.[33,34)] Generally, for a cyclic mechanism, with a rate-determining C–H bond cleavage, the $k_H/k_D$ values were fairly high, as seen from the oxidation of alcohols by various oxidants (Table 6).[19,35—37)] The zero point energy values indicated that the C–H bond was considerably stretched in the transition state,[38)] supporting a cleavage of the carbon–hydrogen bond.

Table 6. Kinetic Isotope Effects for the Oxidation of Primary and Secondary Alcohols by different Oxidants

| Alcohol | Oxidant | $k_H/k_D$ | Zero point energy (kJ mol$^{-1}$)[f)] |
|---|---|---|---|
| Cyclohexanol | V(V) | 4.5[a)] | 3.8 |
| Isopropanol | Cr (VI) | 7.0[b)] | 5.9 |
| Ethanol | PCC | 5.7[c)] | 4.8 |
| Propanol | PCC | 6.7[d)] | 5.6 |
| Cyclohexanol | QDC | 5.8[e)] | 4.8 |

a) Ref. 19; b) Ref. 35; c) Ref. 36; d) Ref. 37; e) This work; f) Ref. 38; pcc (pyridinium chlorochromate).

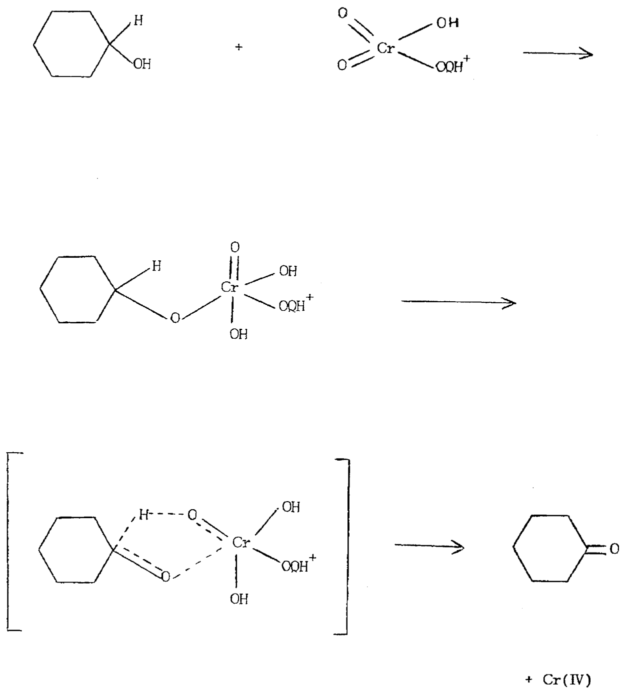
Table 7. Relative Rates of Oxidation of Cyclic Alcohols (0.01 M) by QDC (0.001 M) at 323 K

| Cyclic alcohol | Relative rate |
|---|---|
| Cyclopentanol | 1.9 |
| Cyclohexanol | 1.0 |
| *cis*-4-*t*-Butylcyclohexanol | 1.0 |
| *trans*-4-*t*-Butylcyclohexanol | 1.0 |
| Cycloheptanol | 3.6 |
| Cyclooctanol | 4.7 |

A cyclic transition state could be postulated on the basis of the relative rates of oxidation of the cyclic alcohols studied (Table 7). It was significant that the relative rates of oxidation for the three substrates (cyclohexanol, *cis*- and *trans*-4-*t*-butylcyclohexanol) were equal. With a linear transition state, the cis isomer having an axial hydroxyl group should react faster with QDC than the trans isomer having an equatorial hydroxyl group, the approach of QDC to the latter being more difficult. The similar reactivity of this epimeric pair of alcohols supports a transition state in which the accessibility of both, the hydrogen and the hydroxyl group at the reaction center, are about equally important. It is pertinent to observe that the oxidation of the same pair of alcohols by molecular bromine[39)] or *N*-bromosuccinimide[40)] occurs with a similar conformational insensitivity attributed to the cyclic nature of the transition state.

A stoichiometric conversion of the cyclic alcohols to the corresponding ketones was observed, and this process involved the change CHOH → C=O. If the reaction intermediate were to be visualized as having a cyclic structure, then this would explain all the features of the oxidation reaction. The negative entropy of activation would be consistent with the formation of a cyclic transition state in a bimolecular reaction. The similarity of $\Delta G^{\neq}$ values arises due to the changes in $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values, and stresses the probability that these oxidation reactions involve similar rate determining steps. Using Exners's criterion,[41)] a linear correlation ($r=0.993$) was observed between the activation enthalpies and entropies. The isokinetic temperature was 433 K. Without attaching much physical significance to isokinetic temperatures, it is sufficient to state that a linear trend between the enthalpies and entropies of activation would indicate that the reaction was controlled by both parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$).

If the chromium were to be coordinated through the alcohol O–H group, then the process of electron transfer could take place through the C–O–Cr bond. This would not only facilitate the formation of the chromate ester, but would also enhance the ease of conversion to the ketone. The observed kinetic isotope effect ($k_H/k_D=5.8$) indicated a cleavage of the carbon–hydrogen bond in the rate-determining step, similar to observations reported earlier.[19,35—37)] The proton is removed in the cyclic transition state (in which there would be the coplanarity of all the atoms involved), the center of which resides on an electron-dense oxygen in the chromate ester.[42)] Such a transition state would envisage the transfer of electrons towards the chromium occurring by the formation of the carbon–hydrogen–oxygen bonds as well as the carbon–oxygen–chromium bonds. Partly occupied orbitals are thus used to bind the transferred hydrogen to both carbon and oxygen in the transition state. A cyclic transition state



Scheme 1.

has been suggested as the most plausible intermediate for the oxidation of secondary alcohols by $Cr^{VI}$ reagents.[43] Moreover, this electrocyclic mechanism for the oxidation of cyclic alcohols by QDC involves six electrons, and being a Hückel-type system ($4n+2$), this would be an allowed process.[44]

The reaction sequence (Scheme 1) involving the formation of the chromate ester intermediate satisfactorily explains the observed kinetic data. The ester would be better stabilized in the presence of solvents of low polarity. That is, a decrease of solvent polarity would accelerate the rate of oxidation (Table 4). Further, the small variation in the reaction rate for the oxidation of cyclic alcohols by QDC (Table 7) can also be reconciled with the ester mechanism, since the chromate ester formation is likely to be little influenced by structural changes.[45]

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