

# Solvent effects on the rate of the keto-enol interconversion of 2-nitrocyclohexanone

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**Table 1.** UV-determined tautomeric constants,  $K_T$ , of 2-NCH in several organic solvents and their binary mixtures and selected descriptors of solvent polarity.

| Solvent                          | $K_{T(\text{UV})}$ | $\epsilon$ | $\delta_H$ | $\alpha$ | $\beta$ | $\pi^*$ | $E_T(30)$ | $T_N$ |
|----------------------------------|--------------------|------------|------------|----------|---------|---------|-----------|-------|
| $C_6H_{12}$                      | 6.46               | 2.0        | 8.2        | 0.000    | 0.000   | 0.000   | 30.9      | 0.03  |
| $CCl_4$                          | 5.97               | 2.2        | 8.6        | 0.000    | 0.100   | 0.280   | 32.4      | 0.25  |
| $CHCl_3$                         | 1.92               | 4.8        | 9.3        | 0.200    | 0.100   | 0.580   | 39.1      | 0.67  |
| $CH_2Cl_2$                       | 0.78               | 8.9        | 9.7        | 0.130    | 0.100   | 0.820   | 40.7      | 0.67  |
| $CH_3CN$ - $CH_2Cl_2$<br>(20:80) | 0.39               | 13.7       | 10.1       | 0.142    | 0.160   | 0.806   | 41.7      | 0.67  |
| $CH_3CN$ - $CH_2Cl_2$<br>(50:50) | 0.22               | 21.7       | 10.8       | 0.160    | 0.250   | 0.785   | 43.2      | 0.67  |
| $CH_3CN$ - $CHCl_3$<br>(80:20)   | 0.14               | 28.8       | 11.3       | 0.192    | 0.340   | 0.716   | 44.3      | 0.67  |
| $CH_3CN$ - $CH_2Cl_2$<br>(80:20) | 0.14               | 30.7       | 11.4       | 0.178    | 0.340   | 0.764   | 44.6      | 0.67  |
| $CH_3CN$                         | 0.12               | 35.9       | 11.8       | 0.190    | 0.400   | 0.750   | 45.6      | 0.67  |

**Table 2.** Sensitivity of the selected descriptors of solvent polarity to different solute-solvent interactions.

| Descriptor                  | solute-solvent interactions   |
|-----------------------------|---|
| $\epsilon$                  | pure aspecific (dipole-dipole and ion-dipole) electrostatic interactions  |
| $\delta_H$                  | cavitation energy interactions  |
| $E_T(30)$ , $\pi^*$ , $T_N$ | aspecific (dispersive and electrostatic) and specific (hydrogen bonding and/or lone pair donor-acceptor) interactions |
| $\alpha$                    | H-bond donor specific interactions  |
| $\beta$                     | H-bond acceptor specific interactions   |

**Table 3.** Second order rate constants,  $k_{app}^{TEA}$ ,  $k_1^{TEA}$  and  $k_{-1}^{TEA}$  for the base catalyzed keto-enol interconversion of 2-NCH in aprotic solvents at different temperatures.

| Solvent                         | T (°K) | $k_{app}^{TEA} (M^{-1}s^{-1})$ | $k_1^{TEA} (M^{-1}s^{-1})$ | $k_{-1}^{TEA} (M^{-1}s^{-1})$ | $\Delta G^\ddagger (Kcal mol^{-1})$ | $K_T$ |
|---------------------------------|--------|--------------------------------|----------------------------|-------------------------------|-------------------------------------|-------|
| CHCl <sub>3</sub>               | 288.15 | 25.7 (± 0.7)                   | 17.4                       | 8.30                          | 13.3                                | 2.10  |
|                                 | 293.15 | 29.6 (± 0.4)                   | 19.8                       | 9.80                          | 13.5                                | 2.01  |
|                                 | 308.15 | 39.2 (± 0.4)                   | 24.9                       | 14.3                          | 13.9                                | 1.75  |
|                                 | 313.15 | 44.0 (± 0.8)                   | 27.5                       | 16.5                          | 14.0                                | 1.66  |
| CH <sub>2</sub> Cl <sub>2</sub> | 283.15 | 49.8 (± 0.9)                   | 22.2                       | 27.6                          | 14.3                                | 0.805 |
|                                 | 288.15 | 61.8 (± 4.3)                   | 27.4                       | 34.4                          | 14.5                                | 0.797 |
|                                 | 303.15 | 108 (± 2)                      | 47.1                       | 60.9                          | 14.9                                | 0.773 |
|                                 | 308.15 | 116 (± 3)                      | 50.3                       | 65.7                          | 15.1                                | 0.765 |
| CH <sub>3</sub> CN              | 283.15 | 299 (± 5)                      | 27.2                       | 272                           | 15.0                                | 0.100 |
|                                 | 288.15 | 343 (± 6)                      | 32.0                       | 311                           | 15.2                                | 0.103 |
|                                 | 303.15 | 633 (± 33)                     | 64.8                       | 568                           | 15.8                                | 0.114 |
|                                 | 308.15 | 752 (± 136)                    | 78.8                       | 673                           | 16.0                                | 0.117 |

**Table 4.** Second order rate constants,  $k_{app}^{Pyr}$ ,  $k_1^{Pyr}$  and  $k_{-1}^{Pyr}$  for the base catalyzed keto-enol interconversion of 2-NCH in aprotic solvents and their binary mixtures at different temperatures.

| Solvent           | T (°K) | $10^{-2} k_{app}^{Pyr} (M^{-1}s^{-1})$ | $10^{-2} k_1^{Pyr} (M^{-1}s^{-1})$ | $10^{-2} k_{-1}^{Pyr} (M^{-1}s^{-1})$ | $\Delta G^\ddagger (Kcal mol^{-1})$ | $K_T$ |
|-------------------|--------|--|------------------------------------|---------------------------------------|-------------------------------------|-------|
| CHCl <sub>3</sub> | 288.15 | 0.84 (± 0.02)                          | 0.57                               | 0.27                                  | 19.6                                | 2.10  |
|                   | 293.15 | 1.1 (± 0.1)                            | 0.70                               | 0.40                                  | 19.8                                | 2.01  |
|                   | 303.15 | 1.9 (± 0.1)                            | 1.2                                | 0.70                                  | 20.2                                | 1.84  |
|                   | 308.15 | 2.2 (± 0.1)                            | 1.4                                | 0.80                                  | 20.4                                | 1.75  |
|                   | 313.15 | 2.8 (± 0.2)                            | 1.7                                | 1.1                                   | 20.6                                | 1.66  |
|                   | 318.15 | 3.4 (± 0.1)                            | 2.1                                | 1.3                                   | 20.8                                | 1.58  |

|                                 |        |               |      |      |      |       |
|---------------------------------|--------|---------------|------|------|------|-------|
| CH <sub>2</sub> Cl <sub>2</sub> | 283.15 | 0.83 (± 0.02) | 0.37 | 0.46 | 19.6 | 0.805 |
|                                 | 293.15 | 1.6 (± 0.1)   | 0.70 | 0.90 | 19.2 | 0.797 |
|                                 | 303.15 | 2.5 (± 0.1)   | 1.1  | 1.4  | 20.0 | 0.773 |
|                                 | 308.15 | 3.5 (± 0.2)   | 1.5  | 2.0  | 20.1 | 0.765 |
| CH <sub>3</sub> CN              | 313.15 | 4.3 (± 0.1)   | 1.9  | 2.4  | 20.3 | 0.757 |
|                                 | 288.15 | 5.8 (± 0.1)   | 0.54 | 5.3  | 18.5 | 0.103 |
|                                 | 303.15 | 13 (± 1)      | 1.3  | 12   | 19.0 | 0.114 |
|                                 | 308.15 | 19 (± 1)      | 2.0  | 17   | 19.1 | 0.117 |
|                                 | 318.15 | 29 (± 2)      | 3.2  | 26   | 19.4 | 0.124 |