Acta Chemica Scandinavica B 31 (1977) 302—306

# Tropylium Ions. Part VI.[1] Kinetics of Reactions of 3′,5′-Dialkyl-substituted 4′-Hydroxyphenyltropylium Ions in Aqueous Solution*

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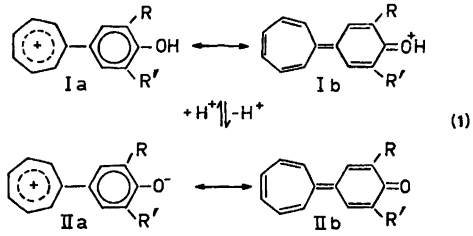
The reactions of 3′,5′-di-*tert*-butyl-substituted and 3′,5′-dimethyl-substituted 4′-hydroxyphenyltropylium fluoroborate in aqueous solutions of different pH have been studied by conventional and stopped-flow spectrophotometry at 25 °C.

The $pK_a$ values found for the dissociation of the two tropylium ions to 2,6-disubstituted 4-cycloheptatrienylidenecyclohexadienones were 4.48 and 6.26, respectively. The $pK_R$ value for the second of the tropylium ions was 5.74.

The first-order rate constants measured from the disappearance of the substituted 4-cycloheptatrienylidenecyclohexadienones in different buffered solutions are minimum values. The rates are discussed in terms of reactions of the tropylium ions and the 4-cycloheptatrienylidenecyclohexadienones with water and hydroxide ion.

The reactivities and stabilities of the studied compounds are compared with those of the corresponding unsubstituted compounds.




(1)

*Scheme 1.*

As early as 1962, van Helden *et al.*[2] found that 4′-hydroxy-3′,5′-dimethylphenyltropylium chloride (the cation of which is I, R = R′ = Me) on heating in dry nitrogen or on basification with sodium hydrogen carbonate yielded a purple pigment (II, R = R′ = Me). The compound was rapidly oxidized to an insoluble material. At the same time and later on, the existence of the parent compound, 4-cycloheptatrienylidenecyclohexadienone (II, R = R′ = H), was observed in solution.[3–5] Attempts to prepare the compound in crystalline form proved unsuccessful, however. On the other hand, the compounds II where R or R and R′ are hydroxy,[4] methoxy,[4,8] *tert*-butyl,[6] bromo [7] or chloro [8] substituents have been reported.

During the course of our studies on tropylium ions we successfully used the stopped-flow technique to follow the reactions of 4′-hydroxyphenyltropylium ion (I, R = R′ = H) and 4-cycloheptatrienylidenecyclohexadienone (II, R = R′ = H) formed from it on basification.[9] To obtain quantitative information about the stabilizing effect of methyl and *tert*-butyl substituents we carried out the study now reported.

## EXPERIMENTAL

*Materials.* 3′,5′-Dimethyl- and 3′,5′-di-*tert* butyl-substituted 4′-hydroxyphenyltropylidene were synthesized from 2,6-dimethylphenol and 2,6-di-*tert*-butylphenol, respectively, and 7-methoxytropylidene in acetic acid (*cf.* Ref. 6). The former was converted to 4′-hydroxy-3′,5′-dimethylphenyltropylium fluoroborate by boiling with an excess of triphenylmethyl fluoroborate in acetonitrile at 70 °C for 1 h. The product was precipitated by adding ethyl acetate and recrystallized from a mixture of acetonitrile and ethyl acetate; the crystals obtained decomposed at 205 °C, UV [water (log

* Presented in part at Third IUPAC Conference on Physical Organic Chemistry, la Grande Motte, France, September 6–10, 1976.

$\varepsilon$)]: 442 (4.21), 272 (4.85) nm ($M^{-1}$ $cm^{-1}$). 4'-Hydroxy-3',5'-di-*tert*-butylphenyltropylium fluoroborate was synthesized analogously. It decomposed at 209 – 211 °C, UV [water (log $\varepsilon$)]: 443, (4.15), 270 (3.82) nm ($M^{-1}$ $cm^{-1}$).

Buffer components were commercial chemicals used without further purification. Water was distilled from potassium permanganate solution under a nitrogen atmosphere.

*Equilibrium constants.* The $pK_a$ values of the hydroxyphenyltropylium ions at 25 °C were calculated from the initial values of stopped-flow traces measured in different buffer solutions at the wavelength of the maximum absorbance of the substituted 4-cycloheptatrienylidenecyclohexadienones. As described earlier,[10] the $pK_R$ value of the 4'-hydroxy-3',5'-dimethylphenyltropylium ion at 25 °C was measured at the wavelength of the maximum absorbance of the tropylium ion and calculated from the plot of $1/[H^+]$ against $1/(A - A_\infty)$. The ionic strength was $1.0 \times 10^{-2}$ M.

*Rate constants.* The first-order rate constants were measured at 25 °C by following the disappearance of a 4-cycloheptatrienylidenecyclohexadienone either by conventional spectrophotometry or by stopped-flow technique, with tropylium ions in perchloric acid solutions mixed with the buffer solutions. The ionic strength was $1.0 \times 10^{-2}$ M except where the pH was so high ($[OH^-] > 10^{-2}$) that this ionic strength was impossible.

*Apparatus.* The stopped-flow apparatus, of Gibson-Durrum type, has been described earlier.[10] The spectra were scanned with a Cary Model 16 spectrophotometer equipped with a specially designed thermostated cell holder. A Cahn Gram Electrobalance was used for weighing small amounts and a Radiometer PHM63 digital pH-meter for pH measurements.

## RESULTS

At 25 °C the $pK_a$ value of the fast proton-transfer reaction (1) was 6.26 for the 4'-hydroxy-

$$C_7H_6+C_6H_2RR'OH+H_2O \rightleftharpoons C_7H_6+C_6H_2RR'O^-+H_3O^+ \quad (1)$$

3',5'-dimethylphenyltropylium ion measured in dihydrogen phosphate – monohydrogen phosphate buffer solutions at 549 nm, and 4.48 for 4'-hydroxy-3',5'-di-*tert*-butylphenyltropylium ion measured in acetic acid – acetate buffer solutions at 510 nm.

The $pK_R$ value of the slower reaction (2)

$$C_7H_6+C_6H_2RR'OH+2\ H_2O \rightleftharpoons HOC_7H_6C_6H_2RR'OH+H_3O^+ \quad (2)$$

could not be obtained for 4'-hydroxy-3',5'-di-*tert*-butylphenyltropylium ion as reaction (1) takes place before reaction (2) in the pH region necessary for measurements. Reaction (1) also interferes with the evaluation of the $pK_R$ value for 4'-hydroxy-3',5'-dimethylphenyltropylium ion, but by working at 442 nm with acetic acid – acetate buffers having pH values from 3.90 to 5.17 we obtained a $pK_R$ value of 5.74 at 25 °C.

The measured rate constants are given in Tables 1 and 2. The reaction of 2,6-di-*tert*-butyl-4-cycloheptatrienylidenecyclohexadienone was preceded by a faster reaction with decreasing absorbance. The rate constants for the latter, measured without taking any reverse reactions into account in the calculations, are given in Table 3.

The rate constant observed from the disappearance of a 4-cycloheptatrienylidenecyclo-

*Table 1.* First-order rate constants measured from the disappearance of 2,6-dimethyl-4-cycloheptatrienylidenecyclohexadienone in aqueous solutions at 25 °C.

| Ionic strength/M | pH | Method [a] | $k_{obs}/s^{-1}$ |
|---|---|---|---|
| NaOH as buffer | | | |
| $2.0 \times 10^{-1}$ | 13.30 | S | 7.9 |
| $5.0 \times 10^{-2}$ | 12.69 | S | 2.1 |
| $2.5 \times 10^{-2}$ | 12.38 | S | 1.0 |
| $1.0 \times 10^{-2}$ | 11.60 | S | $1.9 \times 10^{-1}$ |
| $1.0 \times 10^{-2}$ | 11.18 | S | $5.7 \times 10^{-2}$ |
| Carbonate as buffer | | | |
| $1.0 \times 10^{-2}$ | 10.47 | S | $2.0 \times 10^{-2}$ |
| | 9.88 | C | $8.0 \times 10^{-3}$ |
| Borate as buffer | | | |
| $1.0 \times 10^{-2}$ | 9.60 | C | $2.5 \times 10^{-3}$ |
| | 9.28 | C | $2.0 \times 10^{-3}$ |
| | 8.82 | C | $1.6 \times 10^{-3}$ |
| | 8.62 | C | $1.8 \times 10^{-3}$ |
| | 8.33 | C | $2.0 \times 10^{-3}$ |
| | 7.94 | C | $4.1 \times 10^{-3}$ |
| Phosphate as buffer | | | |
| $1.0 \times 10^{-2}$ | 7.32 | C | $1.4 \times 10^{-2}$ |
| | 6.69 | S | $5.6 \times 10^{-2}$ |
| | 6.64 | S | $6.4 \times 10^{-2}$ |
| | 6.46 | S | $8.4 \times 10^{-2}$ |
| | 6.37 | S | $1.1 \times 10^{-1}$ |
| | 6.13 | S | $1.9 \times 10^{-1}$ |

[a] S = stopped-flow; C = conventional.

*Table 2.* First-order rate constants measured from the disappearance of 2,6-di-*tert*-butyl-4-tropylidenecyclohexadienone in aqueous solutions at 25 °C.

| Ionic strength/M | pH | Method [a] | $k_{obs}/s^{-1}$ |
|---|---|---|---|
| NaOH as buffer | | | |
| $2.0 \times 10^{-1}$ | 13.30 | S | $1.5 \times 10^{-2}$ |
| $5.0 \times 10^{-2}$ | 12.69 | C | $2.9 \times 10^{-3}$ |
| $2.5 \times 10^{-2}$ | 12.38 | C | $9.3 \times 10^{-4}$ |
| $1.0 \times 10^{-2}$ | 11.60 | C | $2.9 \times 10^{-4}$ |
| $1.0 \times 10^{-2}$ | 11.18 | C | $1.8 \times 10^{-4}$ |
| Carbonate as buffer | | | |
| $1.0 \times 10^{-2}$ | 10.53 | C | $1.8 \times 10^{-4}$ |
| | 9.88 | C | $2.0 \times 10^{-4}$ |
| Borate as buffer | | | |
| $1.0 \times 10^{-2}$ | 9.28 | C | $1.6 \times 10^{-4}$ |
| | 8.60 | C | $1.2 \times 10^{-4}$ |
| | 8.28 | C | $1.6 \times 10^{-4}$ |
| | 7.72 | C | $1.5 \times 10^{-4}$ |
| Phosphate as buffer | | | |
| $1.0 \times 10^{-2}$ | 7.32 | C | $1.5 \times 10^{-4}$ |
| | 6.64 | C | $1.3 \times 10^{-4}$ |
| | 6.08 | C | $1.6 \times 10^{-4}$ |
| Acetate as buffer | | | |
| $1.0 \times 10^{-2}$ | 5.47 | C | $2.3 \times 10^{-4}$ |
| | 5.32 | C | $5.6 \times 10^{-4}$ |
| | 4.99 | C | $1.1 \times 10^{-3}$ |

[a] S = stopped-flow; C = conventional.

*Table 3.* First-order rate constants calculated from the fast initial decrease of the absorbance of 2,6-di-*tert*-butyl-4-cycloheptatrienylidene-cyclohexadienone in aqueous solutions at 25 °C. Method: Stopped-flow. Ionic strength: $1.0 \times 10^{-2}$ M.

| Buffer | pH | $k_{obs}/s^{-1}$ |
|---|---|---|
| NaOH [a] | 12.38 | 16 |
| NaOH | 11.18 | 9.6 |
| Carbonate | 10.47 | 8.3 |
| Borate | 8.60 | 4.2 |
| Borate | 7.75 | 3.4 |
| Phosphate | 7.32 | 2.5 |
| Phosphate | 6.64 | 1.4 |

[a] Ionic strength $2.5 \times 10^{-2}$ M.

hexadienone for the reaction of the corresponding tropylium ion with water is given in eqn. (3)

$$k_{obs} = k_w/(1 + K_a/[H^+]) \quad (3)$$

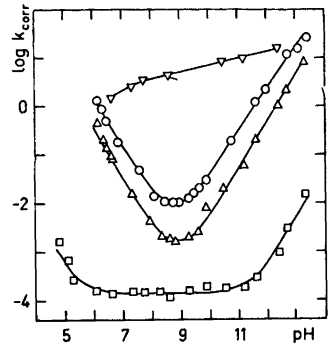



*Fig. 1.* The logarithms of the first-order rate constant measured from the disappearance of unsubstituted (○), 2,6-dimethyl-substituted (△) and 2,6-di-*tert*-butyl-substituted (▽ faster reaction, □ slower reaction) 4-cycloheptatrienylidenecyclohexadienones at 25 °C as functions of pH. The rate constants have been corrected by multiplying by $(1 + [H^+]/K_a)$.

and for the reaction of the tropylium ion with hydroxide ion in eqn. (4).

$$k_{obs} = k_{OH^-}[OH^-]/(1 + K_a/[H^+]) \quad (4)$$

The denominator $(1 + K_a/[H^+])$ in the equations becomes large in buffer solutions of high pH where the concentration of the tropylium ion is less than that of the 4-cycloheptatrienylidenecyclohexadienone.

The observed rate constant for the reactions of a 4-cycloheptatrienylidenecyclohexadienone is given in eqn. (5).

$$k_{obs} = (k'_H + [H^+] + k'_w + k'_{OH^-}[OH^-])/(1 + [H^+]/K_a) \quad (5)$$

The observed rate constants in the acidic range were corrected by multiplying by $(1 + [H^+]/K_a)$, after which the curves in Fig. 1 were drawn from the equation $k_{corr} = 2.5 \times 10^5 [H^+] + 8.0 \times 10^{-4} + 4.8 \times 10[OH^-]$ for dimethyl-substituted compounds and from the equation $k_{corr} = 4.7 \times 10[H^+] + 1.4 \times 10^{-4} + 4.5 \times 10^{-2} [OH^-]$ for di-*tert*-butyl-substituted compounds. The coefficients yielded the values of the rate constants collected in Table 4.

From eqn. (4) follows that $k_{OH^-} = k_{obs}(1 + K_a/[H^+])/[OH^-] \approx k_{obs}K_a/[H^+][OH^-] = k_{obs}K_a/K_w$. Thus $k_{OH^-}$ is $8.0 \times 10^{-4} \times 5.50 \times 10^{-7}/1.01 \times 10^{-14} = 4.4 \times 10^4$ $M^{-1}$ $s^{-1}$ for dimethyl-substituted and $1.4 \times 10^{-4} \times 3.28 \times 10^{-5}/1.01 \times 10^{-14} = 4.6 \times 10^5$ $M^{-1}$ $s^{-1}$ for di-*tert*-butyl-substituted hy-

*Table 4.* Values of $pK_a$ and the rate constants calculated for the reactions of substituted 4-cycloheptatrienylidenecyclohexadienones in aqueous solutions at 25 °C.

| Substituents in 4-cycloheptatrienylidene-cyclohexadienone | $\lambda_{max}$/nm | $pK_a$ | $k'_{H^+}/M^{-1}\,s^{-1}$ | $k'_w/s^{-1}$ | $k'_{OH^-}/M^{-1}\,s^{-1}$ |
|---|---|---|---|---|---|
| None [a] | 525 | 6.83 | $< 1.6 \times 10^6$ | $5.8 \times 10^{-3}$ | $3.2 \times 10^2$ |
| 2,6-Dimethyl | 549 | 6.26 | $< 3.5 \times 10^5$ | $8.0 \times 10^{-4}$ | $4.7 \times 10$ |
| 2,6-Di-*tert*-butyl | 510 | 4.48 | $4.7 \times 10$ | $1.4 \times 10^{-4}$ | $4.5 \times 10^{-2}$ |

[a] Ref. 9.

droxyphenyltropylium ion. The values of $k_w$ were calculated from eqn. (3), using the $k_{obs}$ values in Tables 1 and 2 measured in the most acidic range. The values are collected in Table 5.

The values for the unsubstituted compound differ slightly from the values reported earlier [9] as a result of the present more careful evaluation and of taking into account the effect of the ionic strength on the $pK_a$ of dihydrogen phosphate ion.

The ratio $k'_{H^+}/k'_w$ for di-*tert*-butyl-substituted 4-cycloheptatrienylidenecyclohexadienone is $3.4 \times 10^5$ $M^{-1}$ (Table 4), and close to the value $3.0 \times 10^5$ $M^{-1}$ measured recently for the corresponding reactions of 4-allydidene-2-methoxycyclohexadienone.[13] The same ratio also indicates that the value of $k'_{H^+}$ for the two other compounds in Table 4 is too high and only an arithmetical result as the uncatalyzed hydrolysis of the corresponding tropylium ion is faster.

Critical examination of the rate constants in Table 5 is assisted by the fact that phenyltropylium ions display constant selectivities toward hydroxide ion and water;[10,12,14] *i.e.*, the ratio $k_{OH^-}/k_w$ is constant, about $1.1 \times 10^5$ $M^{-1}$.[10] In any event, on the basis of the values of $k_{OH^-}$ in Table 5, one can conclude that the values for dimethyl- and di-*tert*-butyl-substituted tropylium ions may not be unreasonably high.

## DISCUSSION

The structure of a phenyltropylium ion can be described as a hybrid of canonical forms (*cf.* Scheme 1). Hence, the longest wavelength maximum of the UV spectrum has been found to be strongly dependent upon the substituents on the phenyl ring.[3] As *p*-hydroxy, *m*-*tert*-butyl and *m*-methyl substituents are electron repelling, they produce the bathochromic effects reported in Table 5. Surprisingly, the substituent effects on $pK_R$ in trisubstituted compounds are additive, a feature which is not reflected in the values of the molar absorption coefficient owing to a buttressed substitution.[15]

The structure of a 4-cycloheptatrienylidenecyclohexadienone can likewise be assumed a hybrid of canonical forms (*cf.* Scheme 1). The

*Table 5.* Spectral data, values of $pK_R$ and rate constants calculated for the reactions of substituted 4'-hydroxyphenyltropylium ions in aqueous solutions at 25 °C.

| Substituents in phenyltropylium ion | $\lambda_{max}$/nm | $\varepsilon/M^{-1}\,cm^{-1}$ | $pK_R$ | $k_w/s^{-1}$ | $k_{OH^-}/M^{-1}\,s^{-1}$ |
|---|---|---|---|---|---|
| None [a] | 350 | $1.3 \times 10^4$ | 4.84 | 1.0 | $7.9 \times 10^4$ |
| 4'-Hydroxy [b] | 428 | $1.85 \times 10^4$ | 5.60 | 0.25 | $< 8.5 \times 10^4$ |
| 3',5'-Dimethyl-4'-hydroxy | 442 | $1.63 \times 10^4$ | 5.74 | 0.20 | $\sim 4.4 \times 10^4$ |
| 3',5'-Di-*tert*-butyl-4'-hydroxy | 443 | $1.40 \times 10^4$ | — | — | $\sim 4.6 \times 10^5$ |
| 3'-Methyl [c] | 373 | $1.31 \times 10^4$ | 4.91 | 0.78 | $8.7 \times 10^4$ |
| 4'-Methoxy [c] | 426 | $1.91 \times 10^4$ | 5.61 | 0.27 | $4.3 \times 10^4$ |

[a] Ref. 12, at 23 °C. [b] Ref. 9. [c] Ref. 10.

longest wavelength maximum of the UV spectrum is 525 nm (2.36 eV) for the unsubstituted compound [9] and 510 nm (2.43 eV) and 549 nm (2.26 eV) for the compounds studied here. These values are indicative of a highly unsaturated, conjugated system. In estimating the relative weights of different canonical forms, the wavelength 605 nm (2.05 eV) calculated recently for 4-diphenylmethylidene-1-cycloheptatrienylidene-2,5-cyclohexadiene is pertinent.[16]

On the basis of the data accumulated and the above discussion, we propose that 4′-hydroxyphenyltropylium ions have an electronic structure close to I a and that 4-cycloheptatrienylidenecyclohexadienones have one close to II b.

The fast reaction observed immediately after the basification of di-*tert*-butyl-substituted 4′-hydroxyphenyltropylium ion solutions is noteworthy. Although we cannot at this time offer a clear interpretation of the reaction, we would call attention to the following: (1) the absorbance decreases during the reaction; (2) this decrease is independent of the pH; (3) the rate of the reaction is almost independent of the pH; (4) the reaction was found only in the case of the most stable 4-cycloheptatrienylidenecyclohexadienone studied here.

2,6-Dimethyl-substituted 4-cycloheptatrienylidenecyclohexadienone reacts with hydroxide ion 7 times slower and the 2,6-di-*tert*-butyl-substituted compound 7100 times slower than the unsubstituted compound. This stabilization can be ascribed, at least in the case of *tert*-butyl substituents, mainly to steric effects.

*Acknowledgement.* Financial support of this work by the Science Research Council of Finland is gratefully acknowledged.

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Received October 28, 1976.