two *tert*-butyl groups). *Anal.* Calcd for $C_{16}H_{26}$: C, 88.0; H, 12.0. Found: C, 88.0; H, 11.8.

Product B (21% by vpc) was obtained as a pale yellow oil. It was identified as **2,6-di-*tert*-butyl-1-(2-methyl-3-butenyl)-4-methylbenzene (30)** by its nmr spectrum, which showed singlets at τ 3.14 (2 H, aromatic protons adjacent to *tert*-butyl groups), 7.80 (3 H, aromatic methyl), and 8.60 (18 H, *tert*-butyl groups), a doublet at τ 9.28 (3 H, $J = 6.8$ Hz, methyl group on side chain), and a doublet at τ 6.88 (2 H, $J = 8.3$ Hz, benzylic methylene on side chain) as well as three vinyl protons in the region τ 3.4–5.3. *Anal.* Calcd for $C_{20}H_{32}$: C, 88.2; H, 11.8. Found: C, 88.2; H, 11.8.

Product C (44% yield by vpc) was assigned the structure **2,6-di-*tert*-butyl-1-(*trans*-3-pentenyl)-4-methylbenzene (31)** on the basis of the nmr spectrum, which showed peaks for aromatic hydrogens, an aromatic methyl, and *tert*-butyl groups at essentially the same positions as those in **30**. It also showed a two proton multiplet around τ 6.9 (benzylic methylene group) and around τ 7.8 (allylic methylene group), and a doublet of doublets ($J = 3.5$, 1.5 Hz) at τ 8.35 (3 H, methyl group on a double bond). *Anal.* Calcd for $C_{20}H_{32}$: C, 88.2; H, 11.8. Found: C, 88.0; H, 11.9.

Product D (23% yield by vpc) was obtained as a pale yellow oil and assigned the structure **2,6-di-*tert*-butyl-1-(*cis*-3-pentenyl)-4-methylbenzene (32)** on the basis of its nmr spectrum which showed aromatic hydrogen, aromatic methyl, and *tert*-butyl groups similar to those of **30** and **31**. Its benzylic methylene and allylic methylene absorptions were also essentially identical with those of **31**, but it showed the vinyl methyl group as a doublet of doublets ($J = 5.0$, 1.5 Hz) at τ 8.46.

Rearrangement of Semibenzene 26. Compound **26** (0.17 g) was placed in an nmr tube and heated in an oil bath at 110° overnight. Its vpc on column A at 185° showed the presence of two major components with retention times of 2.1 and 4.7 min, in the area ratio 1:3, and two minor components with retention times of 2.8 and 6.4 min. The major components were isolated by preparative vpc on column B at 190°. The product with a retention time of 2.8 min was identified as compound **27**. The product with a retention time of 4.7 min was obtained as a yellow oil. Its nmr spectrum showed singlets at τ 8.60, 7.79, and 3.12 for the *tert*-butyl groups, aromatic methyl groups, and aryl hydrogens, respectively. It showed a multiplet from τ 3.89 to 4.69 (1 H, secondary vinyl proton), from τ 4.90 to 5.39 (2 H, primary vinyl protons), from τ 7.60–8.12 (2 H, allylic methylene group), and from τ 6.80–7.05 (2 H, benzylic methylene group). This product was assigned the structure **2,6-di-*tert*-butyl-1-(4-pentenyl)-4-methylbenzene (33)**.

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Cation–Anion Combination Reactions. VII.[1] Reactions of Aryltropylium Ions in Aqueous Solution

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Abstract: The reactions of tropylium, phenyltropylium, *p*-chlorophenyltropylium, *p*-methoxyphenyltropylium, and *p*-dimethylaminophenyltropylium ions in buffered aqueous solutions have been studied by stop-flow spectrophotometry. The $\mathrm{p}K_\mathrm{R}$ values and the rate constants for the reactions with water and with hydroxide ion, respectively, are as follows for the various cations: tropylium ion, 4.76, 2.6 sec^{-1}, $3.1 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$; phenyltropylium ion, 4.84, 1.0 sec^{-1}, $7.9 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$; *p*-chlorophenyltropylium ion, 4.55, 1.2 sec^{-1}, $1.4 \times 10^5\ M^{-1}\ \mathrm{sec}^{-1}$; *p*-methoxyphenyltropylium ion, 5.75, 0.27 sec^{-1}, $4.0 \times 10^4\ M^{-1}\ \mathrm{sec}^{-1}$; *p*-dimethylaminophenyltropylium ion, 7.35, 0.020 sec^{-1}, $1.7 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$. Thus, although the stabilities of the cations vary over three powers of ten and the reactivities toward water and hydroxide ion vary by two powers of ten, the selectivities toward water and hydroxide ion are nearly constant.

Tropylium ions have attracted considerable attention over the past decade.[2–6] The $\mathrm{p}K_\mathrm{R}$ value of the tropylium ion in aqueous solution was determined by Doering,[2] and the rate constant for the reaction of tropyl alcohol with hydronium ion has been reported by Zuman[6] and by Eigen.[7] Jutz and Voithenleitner have reported relative $\mathrm{p}K_\mathrm{R}$ values for a number of aryltropylium ions in aqueous acetonitrile solution.[5]

In connection with our studies of nucleophilic reactions with cationic species,[1a] we have now studied the rates and equilibria of reactions of tropylium ion and aryltropylium ions in buffered aqueous solution.

Results

The $\mathrm{p}K_\mathrm{R}$ values determined are reported in Table I. For the aryltropylium ions, spectrophotometric mea-

Table I. $\mathrm{p}K_\mathrm{R}$ and Spectral Data for Tropylium Ions in Aqueous Solution at 23 ± 1° (Ionic Strength = $1.0 \times 10^{-2}\ M$)

Cation	λ_{max}, nm	ϵ, M^{-1} cm^{-1}	$\mathrm{p}K_\mathrm{R}$	Lit.	Buffer used
$C_7H_7^+$	276	4.1×10^3	4.76	4.75[a] 4.01[b]	Acetate
$C_6H_5C_7H_6^+$	350	1.3×10^4	4.84	3.88[b]	Acetate
p-$ClC_6H_4C_7H_6^+$	377	1.7×10^4	4.55	3.30[b]	Acetate
p-$CH_3OC_6H_4C_7H_6^+$	425	1.8×10^4	5.75	4.60[b]	γ-Picoline
p-$(CH_3)_2NC_6H_4C_7H_6^+$	569	3.8×10^4	7.35	6.90[b]	γ-Collidine

[a] Value determined in aqueous solution by Doering, ref 2.
[b] Values determined in aqueous acetonitrile by Jutz, ref 5.

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surement of the absorbance of the cation in various buffers served to determine the pK_R values. For tropylium ion, the cation and alcohol have strongly overlapping spectra, with isosbestic points at 269 and 292 nm. In this case, absorbance at the 269-nm isosbestic point, at 276 nm, the cation peak, and at 257 nm, the alcohol peak, were treated simultaneously to obtain the pK_R value.

The value of 4.76 for the pK_R of tropylium ion found in this study is in excellent agreement with the value of 4.75 reported by Doering.[2] The values found for the aryltropylium ions cannot be compared with any previous values since the previous data were obtained in an entirely different solvent.[5] The precision in our determinations was better than 0.05 pK unit, and there is no reason to suspect that the accuracy is any worse.

Pseudo-first-order rate constants for the disappearances of the cations in buffered aqueous solution, over a range of pH, were determined by stop-flow spectrophotometry. In all cases, the pH was high enough that only the forward reactions of eq 1 and 2 contributed to

$$R^+ + H_2O \underset{k_{-H_2O}}{\overset{k_{H_2O}}{\rightleftharpoons}} ROH + H^+ \tag{1}$$

$$R^+ + OH^- \underset{k_{-OH}}{\overset{k_{OH}}{\rightleftharpoons}} ROH \tag{2}$$

the observed rates. The data are reported in Table II. Weighted least-squares[8] treatments of the data correlated by eq 3 give the values for k_{H_2O} and k_{OH} reported in the table. The last column of Table II contains the values of the calculated pseudo-first-order rate constants, which indicate the precision of the data.

$$k_{obsd} = k_{H_2O} + k_{OH}(OH^-) \tag{3}$$

Generally, the precision of the rate constants observed and the fits of the data to eq 3 are better than ±10%, and we believe that the accuracy of the derived rate constants is nearly as good.

With the rate and equilibrium constants reported in Tables I and II, eq 4 enables us to calculate the rate

$$K_R = k_{H_2O}/k_{-H_2O} \tag{4a}$$

$$K_{OH} = K_R/10^{-14}M^2 = k_{OH}/k_{-OH} \tag{4b}$$

constants for first-order and second-order (acid-catalyzed) dissociations of the tropyl alcohols reported in Table III.

The value of 1.5×10^5 M^{-1} sec^{-1} for the rate constant for acid-catalyzed dissociation of tropyl alcohol is in rather poor agreement with the value of 2.0×10^6 M^{-1} sec^{-1} reported by Zuman[6] and the value of 6.6×10^4 M^{-1} sec^{-1} reported by Eigen.[7] It is possible that differences in temperatures and ionic strengths could account for the differences. The value reported by Eigen was obtained at 12° and 0.1 M ionic strength whereas our value is for 23° and 0.01 M ionic strength. Zuman apparently used an ionic strength of 0.1–1.0 M, but does not report the temperature for his studies. The accuracy of the values reported in Table III should be comparable to the accuracy of the values for the reverse rate constants reported in Table II. Thus, we believe it unlikely that our values could be in error by more than *ca.* 10%.

Table II. Reactions of Tropylium Ions in Aqueous Solution at 23 ± 1°

Buffer (ionic strength, M)	(OH^-), M	$k_{obsd}{}^a$	$k_{calcd}{}^a$
Tropylium Ion: $k_{H_2O}{}^a = 2.6$; $k_{OH}{}^b = 3.1 \times 10^5$			
Borate (1.0×10^{-2})	9.2×10^{-7}	2.6	2.6
	9.2×10^{-7}	3.3	2.6
	3.6×10^{-6}	4.2	3.7
	7.1×10^{-6}	6.2	4.8
	2.5×10^{-5}	9.2	10.3
	3.0×10^{-5}	9.8	11.9
	5.0×10^{-5}	14.8	18.1
	5.2×10^{-5}	19.0	18.6
	5.5×10^{-5}	16.0	19.6
	5.8×10^{-5}	19.0	20.6
	6.0×10^{-5}	22.0	21.2
	8.2×10^{-5}	27.0	28.0
	8.7×10^{-5}	29.0	29.6
(5.0×10^{-2})	7.8×10^{-5}	23.0	26.8
	1.1×10^{-4}	35.0	33.6
Phenyltropylium Ion: $k_{H_2O}{}^a = 1.0$; $k_{OH}{}^b = 7.9 \times 10^4$			
Borate (1.0×10^{-2})	5.0×10^{-8}	0.89	1.0
	2.2×10^{-6}	1.2	1.2
	6.8×10^{-6}	1.8	1.5
	1.4×10^{-5}	2.8	2.1
	2.6×10^{-5}	3.8	3.0
	5.0×10^{-5}	6.1	4.9
	6.0×10^{-5}	4.6	5.7
	6.6×10^{-5}	6.0	6.2
	7.8×10^{-5}	7.3	7.2
(5.0×10^{-2})	1.1×10^{-4}	9.5	9.6
(1.0×10^{-2})	1.3×10^{-4}	11.5	11.7
(5.0×10^{-2})	1.9×10^{-4}	15.5	16.4
	7.8×10^{-5}	7.6	7.2
p-Chlorophenyltropylium Ion: $k_{H_2O}{}^a = 1.2$; $k_{OH}{}^b = 1.4 \times 10^5$			
γ-Collidine (1.0×10^{-2})	9.3×10^{-7}	1.3	1.3
	9.3×10^{-7}	1.3	1.3
	3.5×10^{-7}	1.2	1.2
	1.5×10^{-7}	1.2	1.2
	1.8×10^{-8}	1.1	1.2
Borate (1.0×10^{-2})	2.6×10^{-6}	1.7	1.6
	3.5×10^{-6}	1.7	1.7
	1.1×10^{-5}	3.2	2.7
	1.4×10^{-5}	3.9	3.2
	2.3×10^{-5}	4.1	4.4
	3.8×10^{-5}	5.9	6.5
p-Methoxyphenyltropylium Ion: $k_{H_2O}{}^a = 0.27$; $k_{OH}{}^b = 4.0 \times 10^4$			
	2.6×10^{-6}	0.37	0.37
	1.1×10^{-5}	0.75	0.71
	1.4×10^{-5}	0.91	0.83
	2.3×10^{-5}	1.1	1.2
	3.8×10^{-5}	1.6	1.8
$(C_2H_5)_3N$ (1.0×10^{-2})	7.6×10^{-5}	3.3	3.3
	4.2×10^{-4}	17.4	17
	6.0×10^{-4}	25.3	24
p-Dimethylaminophenyltropylium Ion: $k_{H_2O}{}^a = 0.020$; $k_{OH}{}^b = 1.7 \times 10^3$			
Borate (1.0×10^{-2})	1.4×10^{-5}	0.041	0.040
	3.8×10^{-5}	0.057	0.083
$(C_2H_5)_3N$ (1.0×10^{-2})	7.6×10^{-5}	0.19	0.15
	4.2×10^{-4}	0.79	0.73
	6.0×10^{-4}	1.2	1.1
	9.8×10^{-4}	1.6	1.7
	1.5×10^{-3}	2.7	2.6
	2.1×10^{-3}	3.3	3.6
	2.6×10^{-3}	4.1	4.4

[a] First-order rate constants in units of sec^{-1}. [b] Second-order rate constants in units of M^{-1} sec^{-1}.

Although the reactions of the aryltropylium ions have been shown to be analogous to the reactions of tropylium ions both by previous[4,5] and the present works, there remains the problem that four possible

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[8] Since the stop-flow technique gives a nearly constant percentage error, the sum of the squares of the quantity $(k_{obsd} - k_{calcd})/k_{obsd}$ is minimized.

Table III. Rate and Equilibrium Constants at 26 ± 1° for $X\text{-}C_7H_6^+$ Reactions

X	K_R, M	$k_{-H_2O}{}^b$ $(\times 10^{-5})$	$k_{-OH}{}^a$ $(\times 10^{4})$	$k_{OH}/k_{H_2O}{}^c$ $(\times 10^{-5})$
H	1.75×10^{-5}	1.5	1.8	1.2
C_6H_5	1.45×10^{-5}	0.69	0.54	0.79
p-ClC_6H_4	2.82×10^{-5}	0.43	0.50	1.2
p-$CH_3OC_6H_4$	1.78×10^{-6}	1.5	2.2	1.5
p-$(CH_3)_2NC_6H_5$	4.47×10^{-8}	4.5	3.8	0.85

[a] Units of sec^{-1}. [b] Units of M^{-1} sec^{-1}. [c] Ratio of the rate constants for reactions of the cations with water and hydroxide ion; units of M^{-1} since k_{H_2O} is a pseudo-first-order constant.

isomeric alcohols can be formed from the substituted tropylium ions. The isomeric composition of the products has not been studied either in previous or the present works. Thus, both rate and equilibrium constants refer to the formation of an unknown isomer distribution and comparisons of values for the different cations cannot be interpreted with confidence.

Discussion

In our view, the most interesting feature of the present data is the near constancy of k_{OH}/k_{H_2O} for the various cations, as shown in the last column of Table III. This constancy is at odds with current concepts of stability-selectivity relationships in carbonium ion chemistry,[9-11] but is in accord with our previous findings concerning nucleophilic reactivities toward cationic species.[1,12]

Using data obtained from azide ion trapping of solvolysis intermediates, both Sneen[9] and Schleyer[11] have shown that the selectivity of the intermediate varies with the reactivity of the reactant. We have shown,[1] however, that more than one intermediate is being trapped in at least some of the solvolysis reactions, and, therefore, that the selectivity observed does not directly pertain to carbonium ion intermediates.

Scott[10] has also argued in favor of a selectivity-reactivity relationship in solvolysis reactions, but support of the proposed relationship with data from reactions of stable carbonium ions was based on extremely limited data. The more extensive data now available from the previous papers in the present series dealing with reactions of stable cationic species with a variety of nucleophiles do not support the stability-selectivity relationship, but rather, indicate that the selectivities of triarylmethyl cations, diazonium ions, and the present tropylium ions are very nearly the same although stabilities vary widely.

We are currently extending our studies of tropylium ion reactions to include more of the same nucleophiles whose reactions with other cations we have previously reported. We are also pursuing studies of trapping of solvolysis intermediates in the hope of understanding the source of the reactivity-selectivity relationships in those reactions.

Experimental Section

Materials. Tropylium fluoroborate was prepared from tropilidene (Shell Chemical Co.) as described by Conrow.[13] Spectral properties were in excellent agreement with literature data.[2]

Phenyltropylium fluoroborate was prepared as described by Wilt and Piszkiewicz.[4] Spectral properties were in good agreement with those reported.

***p*-Chloro-, *p*-methoxy-, and *p*-dimethylaminophenyltropylium perchlorates** were prepared according to the method of Jutz and Voithenleitner.[5] Spectral properties and melting points were in good agreement with those reported.

Water was distilled and kept under an argon atmosphere.

Buffer components were reagent grade commercial materials used without further treatment.

Equilibrium Measurements. Buffers were selected to give pH ranges in which the equilibria could be observed, and such that any chance of buffer reactions with the cations was minimized. From previous experience with similar systems, we have found that borate, acetate, and most tertiary amines meet the last criterion. Master solutions of the buffer components (borax-NaOH, acetic acid-NaOH, tertiary amine-HCl) were prepared and mixed to give constant ionic strength of 2.0×10^{-2} M and pH approximate to that desired.

Master solutions of the tropylium salts were prepared in 10^{-3} M perchloric acid solution. Equal volumes of the tropylium salt solution and the appropriate buffer were mixed, the spectra obtained, and the pH of the final solution measured. Spectra were obtained with a Cary Model 14 spectrophotometer using 1-cm cells, and pH was measured with a Beckman Model 1019 pH meter equipped with glass and calomel electrodes and standardized with commercial buffers within one pH unit of that measured.

All measurements were carried out in an air conditioned room maintained at 23 ± 1°.

Kinetic Measurements. Details of the kinetic measurements are analogous to those described previously in which stop-flow techniques have been used.[1,12]

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