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"ONE-ELECTRON" REDUCIBILITY OF THE SUBSTITUTED TROPYLIUM IONS WITH THE CHROMOUS ION

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Recent publications of kinetic studies on the reaction of the stable carbonium ions with nucleophiles1) seem to have renewed interests in the reactivity of the stable carbonium ions. The one-electron reduction of such carbonium ions in solutions, however, has not been investigated kinetically so far and studies for the quantitative estimation of the reducibility of stable carbonium ions in solutions have been restricted to electrochemical ones such as polarography2) and emf measurements of the cells made of the equilibrated solutions of the carbonium ions and the corresponding radicals.3) Thus, we made an attempt to estimate the relative reducibility of a series of the substituted tropylium ions ($R\text{-}C_7H_6^+$; R = H, Me, Et, i-Pr, t-Bu, Ph, Ph_3C) by the use of the kinetic measurements of the one-electron reduction with Cr(II).4)

Reduction of Tropylium Ions with Cr(II).

It was first ascertained that each substituted tropylium ion is rapidly reduced with Cr(II) in 10% HCl5) to give the dimer of the corresponding tropyl radical in more than 95% yield without the formation of any by-product. From the simplicity of the product the reaction is supposed to proceed by a one-electron transfer producing the tropyl radical, which subsequently is subjected to a rapid coupling. At the first step the chloride ion, which is loosely bound to Cr(II) in 10% HCl, would act as a weakly interacting electron-transfer bridge,[6] thus diminishing the steric effect of the substituents.

For kinetic measurements the reaction was carried out in 10% HCl at 25°C for 0.2-1.5 sec by a flow method, and the conversion was determined by ultraviolet spectroscopy of the dimer. The reaction was found to follow good second-order kinetics with respect to each tropylium ion. From the results listed in Table 1, the inductive effect of the substituent apparently controls the reducibility sequence; t-Bu < i-Pr < Et < Me < H < Ph < Ph_3C.

Table 1. Chromous Ion Reduction Rates, Charge-Transfer Bands, Polarographic Half-Wave Potentials and pK_{R^+}'s, of the Substituted Tropylium Ions

Substituent	k_2	C.T.Band [a]		$E_{1/2}$ [b]	pK_{R^+} [c]
		λ_{max}	ν_{max}		
	1/g.ion·sec	mμ	$10^4 cm^{-1}$	V vs. SCE	
None	74.0	540 [d]	1.852	-0.126±0.002	4.3 [e]
Methyl	11.1	513	1.949	-0.187±0.001	
Ethyl	10.3	512	1.953	-0.195±0.004	
Isopropyl	8.22	505	1.980	-0.235±0.002	
t-Butyl	7.98	508 [f]	1.969	-0.215±0.002	5.0
Phenyl	144	543	1.842	-0.090±0.002	4.1 [g]
Trityl	567	550 ~560	1.818 ~1.786	-0.069±0.001	3.6

a) Measured in 1,2-dichloroethane with pyrene as a donor; $[R\text{-}C_7H_6^+] = 2x10^{-3}$ g.ion/l, [Pyrene] = 0.2 M.

b) Measured in acetonitrile, containing $Et_4N^+ClO_4^-$ (0.5 M) as a supporting electrolyte, vs. Ag/AgCl electrode whose potential was found to be -0.162 V vs. SCE.

c) Determined spectrophotometrically in 23% aqueous ethanol.

d) Lit., λ_{max} 535 mμ (Ref. 7a,b).

e) Lit., pK_{R^+}'s, 4.7 (measured in water; Ref. 8) and 4.0 (measured in 50% aqueous acetonitrile; Ref. 9).

f) Lit., λ_{max} 503 mμ (Ref. 7b).

g) Lit., pK_{R^+}, 3.9 (measured in 50% aqueous acetonitrile; Ref. 9).

Correlation of the Reducibility with the Relative Electron Affinity.

For the estimation of the relative electron affinity of the respective tropylium ions, we made use of the measurements of charge-transfer bands observed between the tropylium ions and an aromatic hydrocarbon, pyrene,[7] and also the determination of the polarographic half-wave potentials ($E_{1/2}$) of the ions at a dropping mercury electrode (Table 1). With a given donor molecule, e.g., pyrene, the frequency of the charge-transfer band, ν_{max}, for a series of similar stable carbonium ions is expected to correlate with the electron affinities of the carbonium ions.[7] Plot of reducibility, as expressed by log k_2, against ν_{max} or against $-E_{1/2}$ exhibits a linear correlation between these values (Fig. 1), suggesting that the reactivity of carbonium ions toward Cr(II) mainly reflects the electron affinity inherent to respective ions.

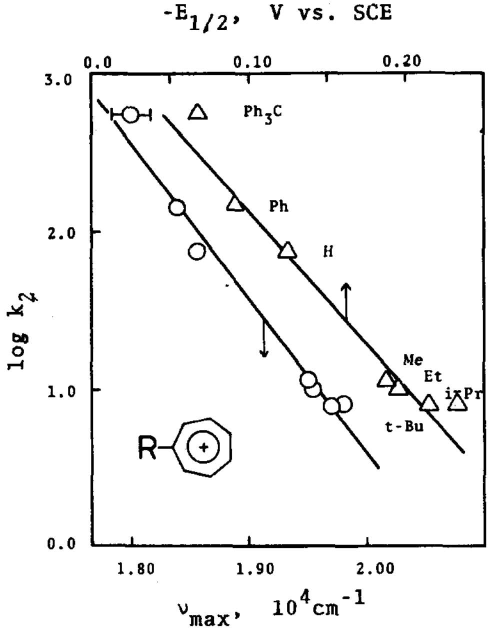

Fig. 1. Correlation of log k_2 with $-E_{1/2}$, and with ν_{max}.

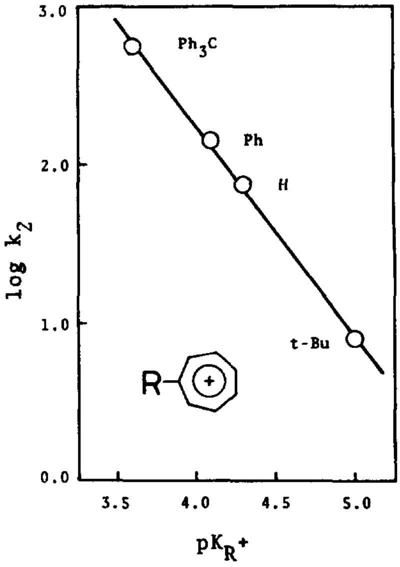

Fig. 2. Correlation of log k_2 with pK_{R^+}.

Correlation of the Reducibility with pK_R+.

The reducibility of the tropylium ions shows a good linear correlation with the stability of respective cations, as expressed by pK_R+ (Fig. 2). Since the equation for pK_R+ is written as Eq. 2 and it can be assumed that the backward reaction is less affected by the structural change, this correlation may imply that the readiness of the carbonium ions to accept one electron is in parallel with the reactivity of the cation toward the electron pair of the nucleophile, e.g., H_2O.

$$R^+ + H_2O \underset{k_b}{\overset{k_f}{\rightleftarrows}} ROH + H^+ \quad (1), \qquad pK_R+ = \log k_b - \log k_f \quad (2)$$

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