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CARBOCATION STABILIZATION BY CYCLOPENTADIENYLDICARBONYLNITROSYLCHROMIUM

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Summary

The pK_{R^+} values for a series of cyclopentadienyldicarbonylnitrosylchromium-substituted carbinyl cations have been determined. These cations have been found to be generally more stable than the structurally-related benzyl cations. Furthermore the results suggest that the dicarbonylnitrosylchromium moiety possesses electron-releasing properties very similar to those of the isoelectronic tricarbonylmanganese system.

Introduction

In 1977 Rausch and coworkers [1] presented evidence from proton and carbon NMR spectra to suggest that the cyclopentadienyldicarbonylnitrosylchromium (cynichrodene) system could effectively stabilize adjacent carbocationic centers. Although many investigations had been made concerning the ability of metallocenes and organometallic systems possessing carbonyl ligands to stabilize carbocations, this was the first system containing a nitrosyl ligand to be examined. The NO ligand is very similar to the CO ligand except that it generally serves as a three-electron donor. Therefore it would be of interest to determine whether metals coordinated to nitrosyl ligands would be better able to stabilize electron-deficient centers than metals coordinated to carbonyl ligands. Conversely the additional electron density supplied to the metal by the ligand might be offset by increased back-bonding.

Since Rausch's data had been qualitative in nature, a study utilizing a quantitative method of determining cation stability was desirable. Measuring the pK_{R^+} values of the carbocations is a facile way of obtaining such information about the thermodynamic stability of the cation. When a carbinol is mixed with a strong acid an equilibrium is established:

$$R^+ + H_2O \overset{K_R}{\rightleftharpoons} ROH + H^+$$

The negative logarithm of the equilibrium constant (K_{R^+}) is the pK_{R^+}. Defined in this manner, the more positive the pK_{R^+} value becomes, the more stable the

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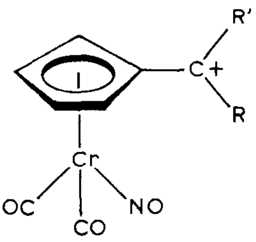


carbocation. The pK_{R^+} values for several organic and organometallic systems are known; thus, a direct comparison between these systems and the cynichrodene system would be possible.

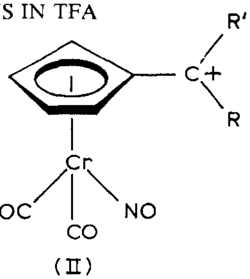
Results and discussion

Following the usual method [2] for the determination of pK_{R^+} values, electronic spectra of the alcohols in various acid-water solutions were recorded. No distinct absorption bands for the alcohols were found to occur above 325 nm in 95% ethanol, but intense bands arising from the cation appeared above 325 nm when concentrated sulfuric or trifluoroacetic acids (TFA) were used as solvents. Rapid decomposition was observed when sulfuric acid solutions were utilized, but the rate of decomposition was much slower when TFA was used. To compensate for this factor the absorbance of the cation was measured at various times and the initial absorption was determined by extrapolation back to time zero. Both the alcohol and the cation were observed to obey Beer's Law over a wide range of concentrations. Quenching the acid solutions with water regenerated the alcohols.

The electronic spectra of the cations and their pK_{R^+} values are recorded in Table 1. When the values of $\log([R^+]/[ROH])$ were plotted versus H_R (i.e., the acidity function for TFA solutions), straight lines with slopes approximately equal to unity

TABLE 1

ELECTRONIC SPECTRA OF CATIONS IN TFA

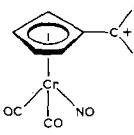


(II)

Compound	R	R′	λ_{max}(nm) (log ϵ)	pK_{R^+}
IIa	H	phenyl	337 (4.12), 444 (3.80)	−8.45
IIb	H	*p*-tolyl	357 (4.18), 473 (4.01)	−8.08
IIc	H	*p*-anisyl	500 (4.14)	−6.96
IId	methyl	phenyl	348 (4.07), 457 (3.75)	−8.24
IIe	phenyl	phenyl	383 (4.29)	−7.35

TABLE 2

pK_{R^+} VALUES OF RELATED ORGANIC AND ORGANOMETALLIC CARBOCATIONS



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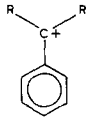

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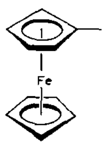

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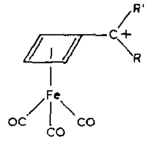

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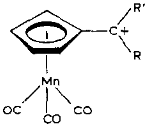

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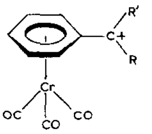

(VII)

Substituents		II	III	IV	V	VI	VII
R	R'						
H	phenyl	−8.45	−13.3 [2]	+0.40 [6]	−3.42 [7]	−8.7 [8]	−10.4 [9]
methyl	phenyl	−8.24	−10.4 [5]	–	−2.89 [7]	−8.3 [8]	
H	*p*-tolyl	−8.08	−11.6 [4]	–	−2.79 [7]	–	−9.4 [9]
phenyl	phenyl	−7.35	−6.6 [2]	+0.75 [3]	−1.46 [7]	−6.5 [8]	–
H	*p*-anisyl	−6.96	−7.9 [4]	+1.37 [3]	−1.72 [7]	–	−5.4 [9]

(0.96–1.05) were obtained for all of the compounds with the exception of the *p*-tolyl derivative. In addition correlation coefficients greater than 0.97 were obtained for all cases studied.

As can be seen, the organic substituents attached to the electron-deficient carbon atom have a significant influence on the overall stability of the cation. In the secondary cations an increase in the electron-donating capability of the aryl system results in a regular increase in the stability of the cation. Generally tertiary cations are more stable than secondary; however, the slightly greater stability of IIc as compared to IIe is probably due to steric factors. Similar results have been reported in the ferrocene system [3].

Table 2 lists pK_{R^+} values for related organic and organometallic systems. As can be seen cations stabilized by the cynichrodene and benzenetricarbonylchromium systems are generally more stable than the corresponding benzyl cations. This suggests that both the tricarbonylchromium and the dicarbonylnitrosylchromium groups are capable of supplying electron-density to the cationic center. The similarities of pK_{R^+} values for the cynichrodene and cymantrene systems suggest that the isoelectronic tricarbonylmanganese and dicarbonylnitrosylchromium moieties have very comparable electronic properties. Attempts to study the molybdenum and tungsten analogs of II were unsuccessful due to the extreme instability of the cations in solution.

Experimental

A Perkin–Elmer R-12B NMR Spectrometer, Perkin–Elmer Model 983 Infrared Spectrophotometer, and Perkin–Elmer Lambda 5 UV/VIS Spectrophotometer were used to obtain the spectral data. The Lambda 5 is equipped with microcomputer electronics and is interfaced with a laboratory computer designed for data storage and manipulation.

The hydroxybenzyl-, 1-hydroxy-1-phenethyl-, and hydroxydiphenymethyl-substituted cynichrodene compounds were prepared as previously reported [10]. The remaining two alcohols were prepared by sodium borohydride reduction of the corresponding ketones. The *p*-anisoyl ketone was prepared by Friedel–Crafts acylation of cynichrodene; whereas the *p*-tolyl ketone was prepared by reaction of *p*-toloylcyclopentadienyl sodium with chromium hexacarbonyl followed by nitrosation with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide [11]. Spectral and analytical data for these new compounds are given below. Elemental analyses were performed by M-H-W Laboratories of Phoenix, Arizona.

(p-Tolyl)cynichrodene carbinol (Ib)

Borohydride reduction of the ketone produced the alcohol as a red oil in 75% yield.

IR (thin film): 3613w, 2020vs, 1950vs, 1703vs cm^{-1}. NMR ($CDCl_3$): δ 2.28 (1H, s, OH), 2.34 (3H, s, Me), 4.95 (3H, ring protons), 5.26 (1H, q, ring proton), 5.42 (1H, s, carbinyl proton), 7.24 (4H, m, phenyl). Anal. Found: C, 55.83;H, 4.11; N, 4.37. $C_{15}H_{13}CrNO_4$ calc: C, 55.73; H, 4.05; N, 4.33%.

(p-Anisyl)cynichrodene carbinol (Ic)

Borohydride reduction of the ketone produced the alcohol as a red oil in 21% yield.

IR (thin film): 3611w, 2023vs, 1950vs, 1709vs cm^{-1}. NMR ($CDCl_3$): δ 2.90 (1H, s, OH), 3.76 (3H, s, OCH_3), 4.92 (3H, m, ring protons), 5.17 (1H, q, ring proton), 5.34 (1H, s, carbinyl proton), 6.71 (2H, d, phenyl), 7.33 (2H, d, phenyl). Anal. Found: C, 53.20; H, 4.02: N, 3.96. $C_{15}H_{13}CrNO_5$ calc: C, 53.10; H, 3.86; N, 4.13%.

pK_{R^+} determinations

Stock solutions of the carbinols (concentrations ca. 5×10^{-2} *M*) were prepared by weighing a sample of the alcohol into a 5 ml volumetric flask and diluting with degassed 95% ethanol. For each system the wavelength of maximum absorption was found by scanning the 500–190 nm region. Owing to the instability of the cationic species, solutions for spectroscopic observation were prepared by injecting 3 μl of stock solution directly into a 1 cm cell containing 3 ml of the appropriate acid solution. (All acid solutions were thoroughly degassed prior to use.) Thirty seconds after the initial injection the absorbance at the fixed peak wavelength was recorded for five cycles at 15 second intervals. These readings were used to plot back to the absorbance at time zero.

The determination of the pK_{R^+} value for the *p*-anisyl-substituted carbocation (IIc) is described in detail. The approximate pK_{R^+} value was determined by

TABLE 3

DETERMINATION OF THE pK_{R^+} VALUE FOR CATION IIc

TFA (%)	H_R	A	$\log([R^+]/[ROH])$	pK_{R^+}
72.6	−6.68	0.302	−0.292	−6.97
73.3	−6.79	0.357	−0.177	−6.97
74.0	−6.90	0.429	−0.035	−6.94
74.8	−7.00	0.496	0.096	−6.90
75.5	−7.09	0.498	0.100	−6.99
			Average	−6.96

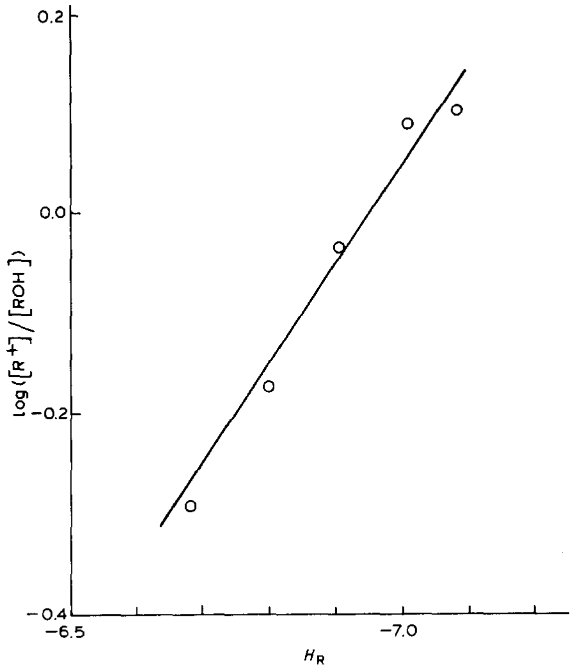

Fig. 1. A plot of log([R^+]/[ROH]) vs. H_R for (*p*-anisyl)cynichrodene carbinol in aqueous trifluoroacetic acid solutions.

examining the UV absorbance at 500 nm for a number of solutions prepared by injecting 3 μl of a 6.52×10^{-5} *M* ethanolic solution of Ic into 3 ml of aqueous TFA solutions of varying concentrations. Following this a minimum of 5 aqueous TFA solutions were prepared which bracketed the approximate concentration required to achieve 50% ionization of the carbinol. Absorbancies at time zero were obtained and pK_{R^+} values were calculated by use of the following equation.

$$pK_{R^+} = H_R + \log([R^+]/[ROH])$$

Values of the acidity function (H_R) for TFA-water solutions have been determined by Stewart [12]. Experimental data is recorded in Table 3 and a plot of the data is shown in Fig. 1.

Acknowledgement

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