Table I. Values of pK_{R^+} for Various Carbonium Ions and Rates of Solvolysis of the Corresponding Aralkyl Chlorides in Aqueous Acetone

Carbonium ion	pK_{R^+}	k_{rel}
Ph_3C^+	-6.6[a]	2.2×10^9 [b]
π-[2,4,6-$(CH_3)_3C_6H_2CH_2$]-[$Cr(CO)_3$]$^+$	-9.3[c]	
π-[$PhCH_2$][$Cr(CO)_3$]$^+$	-11.8[c]	2.2×10^5 [d]
Ph_2CH^+	-13.3,[a] -13.4[c]	6.9×10^4 [d]
2,4,6-$(CH_3)_3C_6H_2CH_2^+$	-17.3,[e] -17.0[c]	
$PhCH_2^+$	<-17.3[e]	(1.00)[d]

[a] Reference 3. [b] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962. [c] This study. [d] Reference 2. [e] N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *J. Am. Chem. Soc.*, **82**, 4719 (1960).

In Table I values of pK_{R^+} ($-\log K$ for the reverse of eq 1) for various carbonium ions and rates of solvolysis of the corresponding aralkyl chlorides are presented. From the pK_{R^+} values one sees that the benzyl cation complexed with tricarbonylchromium is about as stable as the benzhydryl cation and greater than 5.5 pK units more stable than the uncomplexed benzyl cation. The only pK_{R^+} available for a benzyl cation is that for mesityl cation,[8] and comparison of the pK_{R^+} for the free and complexed cation shows that this complexed benzyl cation is stabilized by 7.7 pK units. Comparison of the rates of solvolysis and pK_{R^+} values shows that the rates reflect the stabilities of the carbonium ions in a well-behaved fashion. This correlation of rates of solvolysis and thermodynamic stabilities of the full cations is usually found[9] and is in sharp contrast to the situation found for the rates of solvolysis of α-ferrocenylcarbinyl derivatives and pK_{R^+} values for the corresponding carbonium ions.[10] The results of Hill and Wiesner indicate that the thermodynamic stabilities of the α-ferrocenylcarbonium ions are much greater than predicted by the kinetic data.[10] This suggests that the stabilizing interactions of the tricarbonylchromium moiety with an arenecarbinyl cation differ from those of the cyclopentadienyliron(II) moiety with a cyclopentadienylcarbinyl cation.

The pK_{R^+} values of several *para*-substituted benzyl cations complexed with tricarbonylchromium were measured and are presented in Table II. A very good correlation exists between these data and σ with $\rho = -5.1 \pm 0.5$. A slightly poorer correlation with σ^+ was obtained with $\rho = -2.7 \pm 0.6$. The better correlation with σ than σ^+ suggests that the interaction of the aromatic π system with the carbonium ion in the complexed cation is much different from that found in the free cation or the effective charge on the benzylic carbon has been greatly diminished by the metal.

Table II. Values of pK_{R^+} for *para*-Substituted Benzyl Cations Complexed with Tricarbonylchromium, π-[p-$ZC_6H_4CH_2$][$Cr(CO)_3$]$^+$

Z	pK_{R^+}
MeO	-10.2
Me	-11.0
H	-11.8
Cl	-12.8

It is interesting to note that the effect of the tricarbonylchromium moiety on the stability of the related tropylium ion is much smaller than it is on that of the benzyl cation. The pK_{R^+} values for tropylium ion and (tropylium)tricarbonylchromium ion are 4.7[11] and 6.3,[2] respectively.

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(8) See Table I, footnote *e*.

(9) See Table I, footnote *b*.

(10) E. A. Hill and R. Wiesner, *J. Am. Chem. Soc.*, **91**, 510 (1969).

(11) W. von E. Doering and L. H. Knox, *ibid.*, **76**, 3203 (1954).

(12) American Chemical Society Petroleum Research Fund Graduate Fellow, 1968–1969.

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Arene–Metal Complexes. II. Thermodynamic Stabilities of α-Substituted α-Hydroxybenzyl Cations Complexed with Tricarbonylchromium. The Variable Cation-Stabilizing Ability of the Tricarbonylchromium Moiety[1]

Sir:

In the first part of this series we reported that benzyl cations are significantly stabilized by complexation with tricarbonylchromium.[1a] In this communication we report the effect of the tricarbonylchromium moiety on stabilities of various α-hydroxybenzyl cations. Of special significance is the fact that some of the tricarbonylchromium-complexed cations are less stable than the free ones.

When ethanol solutions of tricarbonylchromium complexes[2] of benzaldehyde, benzophenone, acetophenone, benzoic acid, and N,N-dimethylbenzamide were injected into highly concentrated (87–97%) sulfuric acid, new ultraviolet–visible spectral absorptions were observed. For example, in water the spectrum of complexed benzaldehyde is 213 (30,400),[6] 267 (5940), 320 (8830), and 423 (3400), and in 94.0% sulfuric acid the spectrum obtained is 210 (21,500), 295 (14,700), 333 (4650), and 453 (3920). When the highly colored solutions of these complexes were poured onto ice, the starting complexed benzoyl compounds were recovered. We interpret these facts to mean that, with the possible exception of the amide which may suffer N-protonation,[7] the complexes undergo reversible O-

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(1) (a) Part I: W. S. Trahanovsky and D. K. Wells, *J. Am. Chem. Soc.*, **91**, 5870 (1969); (b) this work was partially supported by Public Health Service Grant GM 13799 from the National Institute of General Medical Sciences; (c) based on work by D. K. W. in partial fulfillment of the requirements for the Ph.D. degree at Iowa State University.

(2) The tricarbonylchromium complexes of benzaldehyde,[3] benzophenone,[4] and benzoic acid[5] were prepared by previously described methods and their melting points agreed with those reported. (Acetophenone)tricarbonylchromium was prepared by the acid-catalyzed hydrolysis of (α-ethoxystyrene)tricarbonylchromium which was prepared by heating the diethyl ketal of acetophenone and hexacarbonylchromium in glyme–butyl ether: mp 86–88° (lit.[5] mp 91.5–92°). The tricarbonylchromium complex of N,N-dimethylbenzamide was prepared by heating the free amide and hexacarbonylchromium in diglyme: mp 96–98°; nmr ($CDCl_3$) δ 5.45 (m, 5) and 3.10 (s, 6). *Anal.* Calcd for $C_{12}H_{11}CrNO_4$: C, 50.53; H, 3.89. Found: C, 50.74; H, 3.93.

(3) G. Drefahl, H.-H. Hörhold, and K. Kühne, *Chem. Ber.*, **98**, 1826 (1965).

(4) J. D. Holmes, D. A. K. Jones, and R. Pettit, *J. Organometal. Chem.*, **4**, 324 (1965).

(5) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

(6) The wavelength is in mμ and the molar extinction coefficient is given in parentheses.

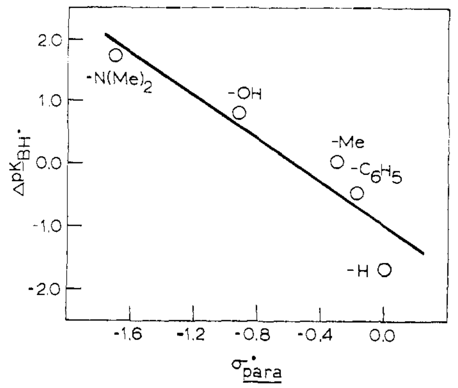
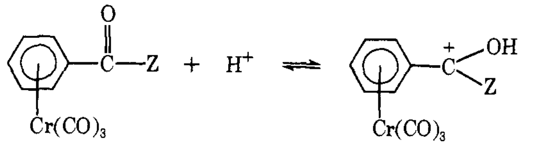


Figure 1. Plot of the differences between the pK_{BH^+} values for the free and complexed benzoyl compounds *vs.* σ^+_p of the α substituent of the benzoyl compound.

protonation to give the corresponding α-hydroxybenzyl cations.



(1)

The basicities of substituted benzaldehydes,[8] acetophenones,[9] benzoic acids,[10] benzamides,[7] and benzophenones[11] have been quantitatively evaluated by determining the pK_{BH^+} ($-\log K$) for the reverse of eq 1 for the conjugate acids of these compounds using spectrophotometric methods and tabulated Hammett acidity function values of aqueous sulfuric acid mixtures.

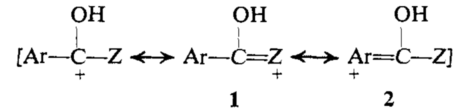
The pK_{BH^+} values for the free and complexed benzoyl compounds which we have determined are presented in Table I. From the ΔpK_{BH^+} values, which are the differences between the pK_{BH^+} values for the free and complexed compounds, it is seen that tricarbonylchromium moiety increases the stability of the conjugate acids of benzaldehyde and benzophenone, has little effect on that of acetophenone, and actually decreases the stability of the conjugate acids of benzoic acid and N,N-dimethylbenzamide.

Table I. Basicity of Free and Tricarbonylchromium-Complexed Benzoyl Compounds

Compd	pK_{BH^+} for free compd[a]	pK_{BH^+} for complex[b]	ΔpK_{BH^+}[c]
C_6H_5CHO	-7.11 (-7.10)[d]	-5.46	-1.65
$C_6H_5COC_6H_5$	-6.13 (-6.18)[e]	-5.68	-0.45
$C_6H_5COCH_3$	-5.91 (-6.15)[f]	-5.96	0.05
C_6H_5COOH	-7.20 (-7.26)[g]	-8.02	0.82
$C_6H_5CON(CH_3)_2$	-1.37 (-1.62)[h]	-3.10	1.73

[a] Maximum error estimated to be ± 0.30 pK unit. [b] Maximum error estimated to be ± 0.50 pK unit. [c] The difference between the free and complexed pK_{BH^+} values. [d] Reference 8. [e] Reference 11 [f] Reference 9. [g] Reference 10. [h] Reference 7.

From Figure 1 it is seen that a fair correlation exists between ΔpK_{BH^+} and the σ^+_p for the carbonyl substituent (slope = -1.72 ± 0.38). A correlation that is



$$[\mathrm{Ar{-}\overset{OH}{\underset{+}{C}}{-}Z} \longleftrightarrow \mathrm{Ar{-}\overset{OH}{C}{=}\underset{+}{Z}} \longleftrightarrow \mathrm{\underset{+}{Ar}{=}\overset{OH}{C}{-}Z}]$$

1 2

almost as good is obtained with σ_p (slope = -3.39 ± 0.88), but a very poor correlation with σ_m was obtained. This suggests that, as resonance structure **1** becomes more important in stabilizing the conjugate acid of the benzoyl compound, resonance structure **2**[12] becomes less important. Thus the electron-withdrawing inductive effect of the tricarbonylchromium[4] becomes more important than the electron-donating ability of the tricarbonylchromium as resonance structure **2** becomes less important. In other words, as the need for stabilization of the benzylic cation by the aromatic system becomes less, the tricarbonylchromium moiety participates less in its stabilization and the ever present electron-withdrawing characteristic of the tricarbonylchromium becomes evident.

The thermodynamic stabilities of the free and complexed benzyl cations and tropylium ion also substantiate the variable cation-stabilizing ability of the tricarbonylchromium group. The complexed benzyl cation is >5.5 pK units more stable than the free cation, but complexed tropylium ion is only 1.6 pK units more stable than the free tropylium ion, which is, of course, much more stable than the free benzyl cation.[1a]

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(8) K. Yates and R. Stewart, *ibid.*, **37**, 664 (1959).

(9) R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **80**, 6355 (1958).

(10) R. Stewart and K. Yates, *ibid.*, **82**, 4059 (1960).

(11) A. Fischer, B. A. Gregor, J. Packer, and J. Vaughen, *ibid.*, **83**, 4208 (1961).

(12) Resonance structure **2** is meant to show delocalization of the positive charge by the free aryl or complexed aryl group and is not meant to imply a mechanism of delocalization of the positive charge by the (aryl)tricarbonylchromium group.

(13) American Chemical Society Petroleum Research Fund Graduate Fellow, 1968–1969.

Further Observations on the Biogenetic-Type Chemistry of the Indole Alkaloids

Sir:

Our previous experiments[1,2] concerning the biosynthesis of the *Aspidosperma* and *Iboga* alkaloids from a *Corynanthe* precursor such as geissoschizine or corynantheine aldehyde in *Vinca rosea* have confirmed the original speculation[3] and the more specific predictions[4] with regard to the identity and oxidation level of the alkaloids involved, many of which had not previously been reported in *V. rosea*. Implicit in the detailed mechanistic proposals[4] is the intervention of the acrylic ester I which serves not only as an isomeric bridge between tabersonine (II) (*Aspidosperma*) and catharanthine (III) (*Iboga*) but also as a rationale for the appearance in nature of racemic alkaloids such as (±)-

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(1) A. A. Qureshi and A. I. Scott, *Chem. Commun.*, 948 (1968).

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(3) E. Wenkert and B. Wickberg, *ibid.*, **87**, 1580 (1965).

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