those reported for other diene–iron carbonyl complexes, so they will serve as the basis for our discussion. The chemical shifts have been considered in most detail, as reviewed by Wilkinson,[3] with attention centered on the large upfield shift of the X_2 protons upon complex formation. The shift assignment of A_2 and X_2 protons has been verified by means of deuterated compounds, so the main question is the relation of the shifts to the nature of the diene–iron bonding. Here the difficulty is that upfield shifts of the X_2 protons can be produced not only by their more or less direct involvement in the diene–iron bonding but also by the magnetic anisotropy of neighboring bonds. In the latter connection, we wish to point out that the anisotropy effects of the CO groups cannot be neglected. The X-ray structural studies have not revealed the proton positions, but the structures found from the heavier atoms[10,11] are such that there could be large upfield CO anisotropy shifts of the X_2 protons and also appreciable ones for the A_2 protons. In brief, there does not appear to be any simple relation between the shifts of the X_2 and A_2 protons and the extent of π-delocalization or localization in the diene complexes.

The situation with respect to the H, H coupling constants is somewhat more favorable because of our better understanding of the relevant structural factors.[12–14] For example, the vicinal H, H coupling is known to be 6–10 c.p.s for *cis* protons in an ethylenic group and 10–18 c.p.s. for *trans*.[12] Thus, the 4.4 c.p.s. value of $J_{AA'}$ and the 8.4 c.p.s. value of J_{AX} and $J_{A'X'}$ are both too small for either the 2,3 or the 1,2 and 3,4 C–C bonds to be normal ethylenic bonds in the complex. But it is an oversimplification to ascribe the differences to delocalization of the π-electrons,[15] because coupling of vicinal protons is dominated by the σ-electron contribution and its angular dependence.[12–14]

It is more instructive to compare the H, H coupling constants in the diene–iron carbonyl complex with those in the heterocyclic five-membered ring compounds[14] such as thiophene, as summarized in Table I. Thiophene was chosen for the comparison because the heteroatom is relatively electropositive and the size of S is not too different from that of Fe. The differences between the two sets of data are surprisingly small, and most of them can be attributed to the diene–iron heterocycle being nonplanar while thiophene is planar. Consider the fact that J_{AX} is larger (8.4 c.p.s.) than $J_{\alpha\beta}$ (5.0 c.p.s.). In the complex, the CCH angles in the H_ACCH_X group probably are smaller than the 125° for thiophene and this would tend to increase J_{AX}.[14] However, as shown in Figure 1, the X-ray structural studies[10,11] make it seem improbable that the group is planar; instead the dihedral angle ϕ between the H_A–C and C–H_X bonds is perhaps 135°, which would make J_{AX} smaller[12] than what it would be if $\phi = 180°$. So, independently of the π-character of the 1,2 and 3,4 C–C bonds, we would not expect J_{AX} to differ greatly from $J_{\alpha\beta}$, as is indeed the case.

TABLE I

COMPARISON OF H, H COUPLING CONSTANTS (C.P.S.) IN THE DIENE–IRON CARBONYL COMPLEX WITH THE CORRESPONDING COUPLING CONSTANTS IN A REPRESENTATIVE HETEROCYCLIC FIVE-MEMBERED RING COMPOUND, THIOPHENE[a]

Diene–iron carbonyl		Thiophene	
J_{AX}	+8.4	$J_{\alpha\beta}$	5.0[b]
$J_{AA'}$	4.4	$J_{\beta\beta'}$	3.3
$J_{AX'}$	−1.7	$J_{\alpha\beta'}$	1.1
$J_{XX'}$	0.0	$J_{\alpha\alpha'}$	2.7

[a] Taken from R. Abraham and H. Bernstein, *Can. J. Chem.*, **37,** 2095 (1959). [b] These values are of the same sign and presumably all are positive: R. Freeman and D. H. Whiffen, *Mol. Phys.*, **4,** 32 (1961), and A. D. Cohen and A. D. McLauchlan, *Discussions Faraday Soc.*, **34,** 132 (1962).

The negative value (−1.7 c.p.s.) found for $J_{AX'}$ is of particular interest in connection with the dependence of the π-electron contribution to the H, H coupling, in the HCC=CH′ fragment, upon the dihedral angle ϕ between the C–H bonds. This has been predicted[13] to be $J_{HH'}^{\pi} = -3.4 \cos^2 (\phi + 90°)$. Thus, for the usual little or no σ-contribution,[13,14] the value observed for $J_{AX'}$ indicates that $90° < \phi \lesssim 135°$, which is compatible with the X-ray structural studies of other diene–iron carbonyl complexes.[10,11] As to the difference between $J_{XX'} \cong 0$ and $J_{\alpha\alpha'} = 2.7$ c.p.s., only the obvious statement can be made; the diene–iron bonding differs in the complex from the diene–S bonding in thiophene.

In summary, it seems fair to say that the n.m.r. data, particularly the H, H coupling constants, are compatible with 1,4 addition of the Fe to the diene to form a nonplanar complex.

Acknowledgments.—We wish to thank Dr. E. Frankel for calling our attention to this problem and for furnishing samples. We are indebted to Dr. W. Derbyshire for his aid with the computer programs.

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(15) This discrepancy is excessively large because both J_{HH}^{cis} and J_{HH}^{trans} increase greatly with decreasing electronegativity of the element directly bonded to a vinyl group. See, *e.g.*, J. S. Waugh and S. Castellano, *ibid.*, **35,** 1900 (1961).

Stability Constants of the Acetylacetone–Chromium(II) Complexes[1a]

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The stability constants of the acetylacetone complexes of all of the divalent cations of the first-row transition elements, except vanadium and chromium,

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(1) (a) Portions of this work were supported by the National Science Foundation. (b) Visiting Associate in Chemistry, California Institute of Technology.

TABLE I

RESPONSE OF E-2 GLASS ELECTRODE

NaOH, M	$-\log[H^+]$ Calcd.	$-\log[H^+]$ Obsd.
0.0100	11.768	11.774 ± 0.004
0.100	12.768	12.767

are known. To extend this work, the complexes formed between acetylacetone and chromium(II) have been studied. A preliminary report of the infrared spectrum and polarographic behavior of the chromium(II)–acetylacetone complex has appeared[2]; the polarographic measurements were made in 40% ethanol and no data regarding the stability constants of the system were obtained. This paper reports the formulas and stability constants of the complexes formed in aqueous solution at ionic strength 1.0.

Experimental

Reagents.—The chromous chloride solution was prepared from an approximately 0.1 F chromic chloride solution containing approximately 0.1 F hydrochloric acid and 0.9 F potassium chloride, the potassium chloride salt being added to maintain a relatively constant ionic strength. It has previously been shown that the formation of chloride complexes of chromium(II) in such media is negligible.[3] The reduction of the chromic ion was accomplished electrolytically as previously described.[4] The chromous content of the solution was determined coulometrically by titration with bromine. Chromous chloride solutions prepared and stored in this manner have been shown to be quite stable.[4] The hydrogen ion concentration was determined in the chromous chloride solution by potentiometric titration with ethylenediamine.

All other chemicals used were reagent grade.

pH Measurements.—The pH measurements were made with a Radiometer Model pHM 4c pH meter, a Beckman Type E-2 glass electrode, and a pressurized, carborundum-frit type saturated calomel electrode (Beckman). All standardizations and titrations were carried out at 25.0°. The meter was first checked for linearity of response using a COHU d.c. voltage standard Model 303B; the standard cell in the meter was calibrated using a Leeds and Northrup Type K-2 potentiometer and a reference set of standard cells. The pH measurements were to be used to determine hydrogen ion *concentration;* therefore the response of the glass–calomel electrode pair to changes in hydrogen ion concentration in solutions of constant ionic strength 1.00 (obtained by the addition of potassium chloride) was checked over the range $-\log[H^+] = 1$ to 13. The calculated and measured concentrations of hydrogen ion of hydrochloric acid–potassium chloride solutions of $-\log[H^+] = 1$ to 3 never differed by more than 0.004 unit. In order to show a linear response between acidic and basic solutions, the value of K_w must be known. The data of Harned and Owen[5] were used to calculate pK_w in 1.00 F KCl; the value obtained was 13.768. The pH meter and electrode pair was calibrated in 0.0100 F HCl ($\mu = 1.0$) and then used to measure the concentration of hydrogen ion in sodium hydroxide solutions with the results shown in Table I. Although there is some scatter in these results, it was concluded that the response of the electrode pair to changes in hydrogen ion concentration was linear over the range $-\log[H^+]$ 1 to 13 and that the pair could therefore be used as a concentration probe. The actual measurements covered a range of only $-\log[H^+]$ 3 to 6. The meter was standardized before each titration with 0.0100 F HCl, and the meter checked afterwards in the same acid; the maximum change noted was 0.006 log unit. On the basis of these standardizations and measurements, the standard deviation of a single measurement was guessed to be ±0.005 log unit.

TABLE II

DATA USED IN CALCULATING FORMATION CONSTANTS

A-7: moles of Cr(II) used 4.84×10^{-5}; moles of acac 1.00×10^{-3}; initial moles of HCl 8.82×10^{-5}; initial volume 50.5 ml. Concentration of NaOH titrant 1.004 F

NaOH, ml.	$-\log[H^+]$	p[acac]	$\bar{n}^a$	$\bar{n}_{\text{calcd}}{}^a$
0.070	3.468	7.113	−0.02	0.07
0.080	3.657	6.926	0.07	0.11
0.090	3.870	6.715	0.19	0.19
0.100	4.090	6.499	0.34	0.30
0.110	4.311	6.281	0.51	0.48
0.115	4.408	6.186	0.60	0.58
0.120	4.500	6.096	0.70	0.69
0.125	4.595	6.004	0.80	0.81
0.130	4.661	5.940	0.90	0.89
0.135	4.748	5.855	1.00	1.01
0.140	4.820	5.785	1.10	1.11
0.145	4.888	5.720	1.20	1.20
0.150	4.968	5.642	1.30	1.30
0.155	5.056	5.556	1.40	1.40
0.160	5.155	5.460	1.50	1.50
0.165	5.271	5.346	1.60	1.61
0.170	5.415	5.204	1.70	1.71
0.175	5.575	5.047	1.80	1.80
0.180	5.780	4.844	1.90	1.87
0.185	6.079	4.547	1.99	1.94

Formation constants calculated: $\log\beta_1 = 5.98$
$\log\beta_2 = 11.72$

A-8: moles of Cr(II) used 4.77×10^{-5}; moles of acac 1.00×10^{-3}; initial moles of HCl 8.70×10^{-5}; initial volume 50.5 ml. Concentration of NaOH titrant 1.004 F

NaOH, ml.	$-\log[H^+]$	p[acac]	$\bar{n}^a$	$\bar{n}_{\text{calcd}}{}^a$
0.070	3.509	7.072	−0.02	0.07
0.080	3.710	6.873	0.07	0.12
0.090	3.940	6.645	0.19	0.20
0.100	4.161	6.428	0.35	0.33
0.110	4.378	6.215	0.53	0.51
0.115	4.475	6.120	0.63	0.62
0.120	4.562	6.035	0.73	0.72
0.125	4.635	5.964	0.83	0.82
0.130	4.715	5.886	0.93	0.93
0.135	4.790	5.814	1.03	1.03
0.140	4.870	5.736	1.13	1.13
0.145	4.949	5.659	1.24	1.24
0.150	5.037	5.573	1.34	1.35
0.160	5.258	5.357	1.54	1.58
0.170	5.520	5.100	1.75	1.76
0.175	5.700	4.922	1.85	1.84
0.180	5.935	4.690	1.94	1.91

Formation constants calculated: $\log\beta_1 = 5.94$
$\log\beta_2 = 11.67$

Average formation constants chosen: $\log\beta_1 = 5.96 \pm .02$
$\log\beta_2 = 11.70 \pm .03$

[a] The average deviation of $\bar{n}$ from $\bar{n}_{\text{calcd}}$ (using the average stability constants) is 0.02.

Results and Discussion

Ionization Constant of Acetylacetone.—Solutions of acetylacetone in 1.00 F potassium chloride were titrated at 25.0° with standard sodium hydroxide. The average value obtained for the ionization constant from four different titrations was $1.325 \pm 0.015 \times 10^{-9}$, giving a value of p$K$ of 8.878 ± 0.007.

***p*H Titrations of the Chromous Ion–Acetylacetone**

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System.—Following the method of Bjerrum[6] in which measurements of the pH of solutions of metal ions and complexing agents may be interpreted to give information concerning the formulas and stability constants of the complexes formed in the system, we find that two complexes are formed between chromium(II) and acetylacetone and have obtained values for the formation constants β_1 and β_2, where

$$\beta_n = \frac{[\mathrm{Cr(acac)}_n{}^{+2-n}]}{[\mathrm{Cr}^{+2}][\mathrm{acac}^-]^n}$$

We assume complexation and ionization reactions in this system to be as follows.

$$\mathrm{Cr}^{+2} + \mathrm{Hacac} \rightleftharpoons \mathrm{Cr(acac)}^+ + \mathrm{H}^+$$
$$\mathrm{Cr(acac)}^+ + \mathrm{Hacac} \rightleftharpoons \mathrm{Cr(acac)}_2 + \mathrm{H}^+$$
$$\mathrm{Hacac} \overset{K_1}{\rightleftharpoons} \mathrm{acac}^- + \mathrm{H}^+$$

In an earlier paper,[4] a similar system has been discussed. Proceeding in an analogous way for this system, we obtain for the average number of ligands bound ($\bar{n}$) per metal ion the expression

$$\bar{n} = \frac{K_1 + [\mathrm{H}^+]}{[\mathrm{H}^+]\Sigma_{\mathrm{Cr}}}\left\{[\mathrm{H}^+] + 2\Sigma_{\mathrm{Cr}} + [\mathrm{K}^+] + [\mathrm{Na}^+] - \frac{K_{\mathrm{w}}}{[\mathrm{H}^+]} - [\mathrm{Cl}^-] - \Sigma_{\mathrm{acac}}\left(\frac{K_1}{K_1 + [\mathrm{H}^+]}\right)\right\}$$

where Σ_{Cr} is the total concentration of Cr(II) and Σ_{acac} is the total concentration of acetylacetone.

Solutions containing chromous chloride and hydrochloric acid were titrated to obtain the formation function of the system. Several attempts were made to form the complex in basic solution, then to titrate the excess base and the complex with standard acid, in this way approaching the equilibrium from the opposite direction. The results were unsatisfactory in that obviously rapid oxidation of the chromous ion occurred in the basic solution, as evidenced by the formation of the violet color of chromic ion.

With all quantities on the right-hand side of the equation easily calculated and the hydrogen ion concentration readily measured, it is possible to calculate $\bar{n}$ and to plot the results *vs.* p[acac]. From this plot the formation constants for the system were obtained using the "correction-term" method of Irving and Rossotti.[7]

This method assumes the formation function is symmetric about $\bar{n} = 1$. The formation curves obtained from many of the titrations were distorted and could not be analyzed in this manner. This was probably due to the oxidation of some of the chromous ion during the titration, as the solutions that gave suspect formation curves were always discolored. Two titrations gave quite symmetric curves from which the successive formation constants of the system could be calculated as $\log \beta_1 = 5.96 \pm 0.02$ and $\log \beta_2 = 11.70 \pm 0.03$. These formation constants were used to calculate a theoretical formation function for the chromium(II)–acetylacetone system and the calculated values are compared with the experimental values in Table II.

Attempts were made to measure the reduction potential of the chromium(II)–acetylacetone complex by direct potentiometry and by polarography. Direct measurements of the potential of a platinum electrode in solutions containing the complex gave wildly erratic results; these are ascribed to the reduction of hydrogen ion at the electrode by the complex. In one instance, bubbles of gas appeared on a clean electrode after a few minutes. Solutions of the complex in near-neutral media do not give polarographic waves at the dropping mercury electrode. Therefore, we can only agree that the complex is a powerful reducing agent, as has previously been stated.[2]

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Correspondence

Five-Coordinate Intermediates in the Base Hydrolysis of Cobalt(III) Complexes[1]

Sir:

The base hydrolysis of complexes of the type $[\mathrm{Co(en)_2AX}]^{n+}$, where en = ethylenediamine, A = OH, Cl, Br, $\mathrm{N_3}$, NCS, $\mathrm{NH_3}$, $\mathrm{NO_2}$, and X = Cl, Br, $\mathrm{NO_3}$, NCS, $\mathrm{N_3}$, have been extensively investigated by Ingold, Nyholm, Tobe, and co-workers,[2] and while their results have been rationalized in terms of an S$_N$2 mechanism involving OH^- attack at the cobalt, the rate law for the reactions is not inconsistent with an S$_N$1CB mechanism.[3] Moreover, the recent isotopic fractionation experiments by Green and Taube[4] on the base hydrolysis of the $[\mathrm{Co(NH_3)_5X}]^{2+}$ system (where X = Cl, Br, $\mathrm{NO_3}$) suggest that this reaction occurs *via* a common intermediate. The result also implies that the observations of Tobe, *et al.*, could be consistent with the production of a five-coordinate intermediate and is particularly relevant when one considers the production of a common intermediate from several different sources, *i.e.*, where the reference group A remains constant and the leaving group varies. Under these circumstances the concentrations of the isomeric products should be independent of the group departed for a particular inter-

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