group, with direction along the MCO bond axis. The total $A_1$ intensity is thus proportional to

$$I_{A_1} = G_{tt}\mu'_{MCO}{}^2(1 + 4\cos^2\theta_1)$$

It is important to distinguish this result from a consideration of the intensities of the individual $A_1$ modes. The highest frequency $A_1$ mode in the $M(CO)_5L$ species is identified with stretching of the four radial CO groups. The lower frequency $A_1$ mode, which is always more intense, is identified with the stretching of the axial CO group. This means that $L_{11} < L_{21}$ in eq 6A. Since $L_{11}$ is not zero, however, the stretching of the axial CO does contribute to the intensity of the highest frequency $A_1$ band. It is incorrect, therefore, to assume that the intensity of the highest frequency $A_1$ mode is determined entirely by the radial stretching.[8] It is possible, however, within the approximation of the local dipole moment derivative, to derive a relationship between intensity ratios and bond angles which does not require a knowledge of the individual $L$ matrix elements. The symmetry coordinates for one component of the E species mode are

$$S_t^{E_a} = \frac{1}{\sqrt{2}}(t_3 - t_5) \qquad S_q^{E_a} = \frac{1}{\sqrt{2}}(q_3 - q_5)$$

By proceeding as above, it can be shown that the intensity of this one component of the E species vibration is

$$I_{E_a} = G_{tt}\mu'_{MCO}{}^2\, 2\sin^2\theta_1$$

The total intensity of the E species absorption is twice this. The ratio $I_{A_1}/I_E$ is thus

$$I_{A_1}/I_E = \frac{1 + 4\cos^2\theta_1}{4\sin^2\theta_1} \tag{8A}$$

Thus the ratio of *total* $A_1$ intensity to the E mode intensity is a function of the angle $\theta_1$, with no assumption regarding the mixing of the two $A_1$ modes. Similar relationships can be derived for other substituted compounds. For example, in an axially-substituted iron pentacarbonyl, $Fe(CO)_4L$, the ratio of total $A_1$ to E species intensity is

$$I_{A_1}/I_E = \frac{1 + 3\cos^2\theta_1}{3\sin^2\theta_1} \tag{9A}$$

The use of such intensity ratios for estimation of bond angles rests on the assumption that stretching of a CO bond in the substance of interest produces a characteristic dipole moment derivative, in the direction of the CO bond axis, which is the same for each MCO group in the molecule.

It is possible to gain an appreciation of the sensitivity of the CO intensities to substitution by considering the total intensity, $I_T$, for each substance over all allowed CO stretching modes. For the $M(CO)_5L$ we have

$$I_T = I_E + I_{A_1} = G_{tt}(4\sin^2\theta + 1 + 4\cos^2\theta)\mu'_{MCO}{}^2$$
$$= 5G_{tt}\mu'_{MCO}{}^2$$

For the parent substance, $M(CO)_6$, assuming the same value for the local dipole moment derivative

$$I_T = 6G_{tt}\mu'_{MCO}{}^2$$

Thus, the ratio of total intensity in the monosubstituted derivative to the total intensity in the unsubstituted compound should be 5:6, if there were no change in the characteristic dipole moment derivative for the MCO group.

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CONTRIBUTION FROM THE CYANAMID EUROPEAN RESEARCH INSTITUTE,
COLOGNY, GENEVA, SWITZERLAND

# Synthesis and Reactivity of Chromium Tricarbonyl Complexes of Substituted Benzoic Esters

BY G. KLOPMAN AND F. CALDERAZZO

*Received December 9, 1966*

Several new *meta*- and *para*-substituted benzoic methyl ester–tricarbonylchromium compounds have been prepared and their rates of alkaline hydrolysis measured at 25° in 56% aqueous acetone. The chromium complexes undergo hydrolysis at considerably higher rates than the corresponding uncomplexed compound. The $\rho$ values for the two reactions are +1.55 and +2.36, thus indicating a lower degree of sensitivity of the chromium complexes to electronic changes in the aromatic ring. The increase in rates for the chromium complexes is explained by a decreased electron density at the electrophilic center. The effect on rates of a $Cr(CO)_3$ group is practically equivalent to that of a *p*-nitro group.

## Introduction

The problem of the reactivity of an aromatic system when bonded to a chromium tricarbonyl moiety has interested a number of investigators in recent years. Ring substitutions and reactions on side chains have been studied. The first group of reactions includes Friedel–Crafts acylations[1-3] and chlorine substitution by $CH_3O^-$ in chlorobenzenetricarbonyl-

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TABLE I

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF SUBSTITUTED BENZOIC METHYL ESTER–TRICARBONYLCHROMIUM COMPOUNDS

| $Cr(CO)_3$ compound | Color | Mp, °C | C, % Calcd | C, % Found | H, % Calcd | H, % Found | Cr, % Calcd | Cr, % Found | Other, % Calcd | Other, % Found | Yield, % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *o*-$CH_3C_6H_4COOCH_3$ | Yellow | 84–85 | 50.36 | 50.53 | 3.52 | 3.60 | 18.17 | 18.11 | | | 31 |
| *m*-$CH_3C_6H_4COOCH_3$ | Yellow | 101–102 | 50.36 | 50.23 | 3.52 | 3.74 | 18.17 | 18.37 | | | 31 |
| *p*-$CH_3C_6H_4COOCH_3$ | Yellow | 104–105 | 50.36 | 50.62 | 3.52 | 3.68 | 18.17 | 18.00 | | | 47 |
| *m*-$C_6H_4(COOCH_3)_2$ | Red-orange | 105–106 | 47.28 | 47.51 | 3.05 | 3.15 | 15.75 | 15.84 | | | 25 |
| *m*-$ClC_6H_4COOCH_3$ | Orange | 76–77 | 43.09 | 43.28 | 2.30 | 2.52 | 16.96 | 16.70 | Cl: 11.56 | 11.50 | 16 |
| *p*-$ClC_6H_4COOCH_3$ | Orange | 103–104 | 43.09 | 43.76 | 2.30 | 2.42 | 16.96 | 16.71 | Cl: 11.56 | 11.53 | 30 |
| *p*-$NH_2C_6H_4COOCH_3$ | Light yellow | 183–184 | 46.00 | 46.10 | 3.16 | 3.37 | 18.10 | 18.09 | N: 4.88 | 5.00 | 35 |
| *p*-$CH_3OC_6H_4COOCH_3$ | Yellow | 101.5–102.5 | 47.69 | 47.81 | 3.33 | 3.55 | 17.20 | 16.92 | | | 33 |
| *o*-$CH_3OC_6H_4COOCH_3$ | Yellow | 106–107 | 47.69 | 47.82 | 3.33 | 3.52 | 17.20 | 16.94 | | | 33 |

chromium.[4] The second type of reaction is comprised of esterifications,[5] alkaline hydrolyses,[5] Claisen condensations,[6] and Cannizzaro[7] and Wittig[8] reactions.

Kinetic data are now available for ring substitutions on chromium tricarbonyl arene derivatives showing that either nucleophilic[4] or electrophilic[9] reactions occur faster on chromium tricarbonyl arene derivatives than on the corresponding uncomplexed aromatic compounds. On the other hand, kinetic data on side-chain reactions of chromium tricarbonyl arene compounds are scarce. Pettit and co-workers[10] have recently published a paper concerning the rate of solvolysis of (benzyl chloride)tricarbonylchromium and (benzhydryl chloride)tricarbonylchromium and found an increase in rates for the complexes compared with the uncomplexed compounds. We now report some kinetic data for the base-catalyzed hydrolysis of a number of substituted methyl benzoate–tricarbonylchromium compounds. In the course of our investigation, we prepared several new chromium tricarbonyl compounds.

## Experimental Section

Melting points are uncorrected. They were measured in capillaries sealed under nitrogen.

Microanalyses are by Dr. K. Eder, Ecole de Chimie, Geneva. Titrimetric determinations were carried out with an automatic Radiometer titrograph, Type SBR2/SBUI/TTA2, with a glass electrode (Radiometer 6202B).

**Preparation of the Compounds.**—The chromium tricarbonyl complexes were prepared by the direct thermal reaction of hexacarbonylchromium with the aromatic esters at atmospheric pressure at 145–200°. The apparatus used, which was very similar to that described by Strohmeier,[11] provided an easy return of the hexacarbonyl from the cold regions of the reaction vessel into the reaction mixture. A nitrogen blanket was maintained during the reaction time. No solvent was necessary in the case of aromatic compounds liquid at room temperature; with solid esters, dilution with di-*n*-butyl ether was used. The reactions were usually run until no more hexacarbonylchromium appeared on the cold regions of the apparatus. After cooling, the reaction mixtures were diluted with dry diethyl ether and filtered over deactivated alumina. The eluates were then evaporated and the solid residues were crystallized from heptane.

The purity of the known compounds—$Cr(CO)_3C_6H_5COOCH_3$[5] and $Cr(CO)_3$-*p*-$C_6H_4(COOCH_3)_2$[12]—was checked by elemental analyses, melting points, and infrared spectra. The new compounds are reported in Table I, together with analytical data and some physical properties.

**Kinetic Measurements.**—All of the kinetic measurements were done in aqueous acetone at 25 ± 0.01°. The solvent contained 400 ml of water made up to 1 l. with acetone (56% of acetone by weight). Equimolar solutions of the ester and NaOH in this solvent were kept separately in a thermostated bath and then rapidly mixed. Samples of the reacting solutions were withdrawn at regular intervals of time and poured into a standardized HCl solution and then titrated back with sodium hydroxide. Since equimolar quantities of the two reagents were used, the simplified kinetic equation, $k = x/ta(a - x)$, could be applied to the experimental values.

Similar procedures were used for the kinetic experiments with both the uncomplexed aromatic compounds and the chromium complexes. In the latter case, however, very dilute solutions had to be used because of the high reaction rates. High reaction rates were, however, desirable in order to minimize the decomposition of the chromium complexes. Although for each kinetic run good plots of $x/(a - x)$ *vs.* time were obtained up to about 50% conversions, the reproducibility of the rate constant values was not always very good. We therefore carried out at least two independent measurements for each compound, except in two cases. In Table II the kinetic results for one of the chromium tricarbonyl complexes are reported to give an idea of the density of points. The rate constants given in Tables III and IV for the uncomplexed ligands and for the chromium complexes, respectively, are averaged values over the indicated number of independent measurements.

TABLE II

ALKALINE HYDROLYSIS OF $Cr(CO)_3C_6H_5COOCH_3$ IN AQUEOUS ACETONE AT 25 ± 0.01° AND AT AN INITIAL CONCENTRATION OF NaOH = $a$ = 0.0025 $M$

| Time, sec | $100x/a$ | $10k$, $M^{-1}$ sec$^{-1}$ |
|---|---|---|
| 93 | 12.7 | 6.26 |
| 145 | 18.7 | 6.35 |
| 230 | 28.0 | [6.76] |
| 336 | 35.0 | 6.41 |
| 463 | 42.0 | 6.25 |
| 629 | 49.7 | 6.28 |
| | Av | 6.31[a] |

[a] Three other runs gave the following values of rate constants: 6.14, 6.28, and 6.31. The average over the four independent measurements is therefore $(6.26 \pm 0.12) \times 10^{-1}$ $M^{-1}$ sec$^{-1}$.

## Results and Discussion

Since we were mainly interested in comparing the reactivity of uncomplexed benzoic methyl esters with

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TABLE III

ALKALINE HYDROLYSIS OF SUBSTITUTED BENZOIC METHYL ESTERS AT 25 ± 0.01° IN 56% AQUEOUS ACETONE

| Substituent | [Reagent], $M$ | No. of runs | $k$, $M^{-1}$ sec$^{-1}$ | | Log $k$ |
|---|---|---|---|---|---|
| $p$-NO$_2$ | 0.0025 | 3 | $(6.40 \pm 0.09) \times 10^{-1}$ | $6.38 \times 10^{-1}$ [a] | −0.1952 |
| | 0.01 | 3 | $(6.36 \pm 0.11) \times 10^{-1}$ | | |
| $p$-COOCH$_3$ | 0.0025 | 3 | $(1.12 \pm 0.02) \times 10^{-1}$ [b] | | −0.9508 |
| $m$-COOCH$_3$ | 0.0025 | 3 | $(5.00 \pm 0.07) \times 10^{-2}$ [b] | | −1.3010 |
| $o$-COOCH$_3$ | 0.025 | 3 | $(1.26 \pm 0.07) \times 10^{-2}$ [b] | | −1.8996 |
| $p$-Cl | 0.0025 | 3 | $(2.45 \pm 0.01) \times 10^{-2}$ | $2.54 \times 10^{-2}$ | −1.5952 |
| | 0.025 | 4 | $(2.61 \pm 0.21) \times 10^{-2}$ | | |
| $m$-Cl | 0.025 | 3 | $(4.28 \pm 0.16) \times 10^{-2}$ | | −1.3686 |
| $o$-Cl | 0.1 | 3 | $(1.26 \pm 0.05) \times 10^{-2}$ | | −1.8996 |
| H | 0.025 | 2 | $(8.06 \pm 0.21) \times 10^{-3}$ | $8.01 \times 10^{-3}$ [c] | −2.0969 |
| | 0.1 | 5 | $(8.00 \pm 0.13) \times 10^{-3}$ | | |
| $p$-CH$_3$ | 0.1 | 3 | $(3.09 \pm 0.09) \times 10^{-3}$ | | −2.5100 |
| $m$-CH$_3$ | 0.1 | 3 | $(4.55 \pm 0.21) \times 10^{-3}$ | | −2.3420 |
| $o$-CH$_3$ | 0.1 | 3 | $(9.00 \pm 0.35) \times 10^{-4}$ | | −3.0458 |
| $p$-NH$_2$ | 0.1 | 3 | $(2.70 \pm 0.08) \times 10^{-4}$ [d] | | −3.5686 |

[a] Reference 13 gives $k = 6.40 \times 10^{-1}$ $M^{-1}$ sec$^{-1}$ under the same conditions. [b] The experimentally determined rate constant was divided by 2 in order to get the value per methyl group. [c] Reference 13 gives $k = 9.01 \times 10^{-3}$ $M^{-1}$ sec$^{-1}$ under the same conditions. [d] Reference 14 gives $k = 2.92 \times 10^{-4}$ $M^{-1}$ sec$^{-1}$ under the same conditions.

that of the corresponding chromium tricarbonyl complexes, the two sets of reactions had to be run under the same experimental conditions.

The values of the rate constants for the alkaline hydrolysis of substituted benzoic methyl esters are reported in Table III. These rate constants have been determined because most of them were unknown in the solvent chosen for the investigation with the chromium complexes. In three cases the rate constants had been measured previously[13,14] and our independent determinations agree well with the values reported in the literature.

The rate constants for the alkaline hydrolysis of the substituted benzoic methyl ester–tricarbonylchromium complexes are reported in Table IV.

TABLE IV

ALKALINE HYDROLYSIS OF SUBSTITUTED BENZOIC METHYL ESTER–TRICARBONYLCHROMIUM COMPLEXES AT 25 ± 0.01° IN 56% ACETONE

| Substituent | [Reagent], $M$ | No. of runs | $k$, $M^{-1}$ sec$^{-1}$ | Log $k$ |
|---|---|---|---|---|
| $p$-COOCH$_3$ | 0.001 | 3 | $3.50 \pm 0.04$ | 0.5441 |
| $m$-COOCH$_3$ | 0.001 | 3 | $1.58 \pm 0.03$ | 0.1987 |
| $p$-Cl | 0.0025 | 3 | $1.28 \pm 0.04$ | 0.1072 |
| $m$-Cl | 0.001 | 2 | $2.23 \pm 0.03$ | 0.3483 |
| H | 0.0025 | 4 | $(6.26 \pm 0.12) \times 10^{-1}$ | −0.2034 |
| $p$-CH$_3$ | 0.0025 | 3 | $(3.13 \pm 0.06) \times 10^{-1}$ | −0.5045 |
| $m$-CH$_3$ | 0.0025 | 4 | $(5.06 \pm 0.07) \times 10^{-1}$ | −0.2958 |
| $o$-CH$_3$ | 0.0025 | 3 | $(1.11 \pm 0.01) \times 10^{-1}$ | −0.9547 |
| $p$-OCH$_3$ | 0.0025 | 1 | $2.16 \times 10^{-1}$ | −0.665 |
| $p$-NH$_2$ | 0.005 | 1 | $2.84 \times 10^{-2}$ | −1.5467 |

No product analysis was done systematically, but in numerous cases the reaction was run over a very long time, and the alkali consumption was checked and found to be very close to the calculated amount. The absence of secondary reactions[15] is also indicated by the previous results[5] showing that the alkaline hydrolysis of $Cr(CO)_3C_6H_5COOCH_3$ followed by acidification gives $Cr(CO)_3C_6H_5COOH$ in almost quantitative yields. Finally it is worth mentioning also that, in the case of the chloro-substituted benzoic methyl ester–chromium tricarbonyl complexes, chlorine replacement by hydroxide ion does not take place to any significant extent under the reaction conditions used. This is again indicated by the consumption of sodium hydroxide over long reaction times and by the results contained in a recent paper[4] on the chlorine replacement by methoxide ions in chlorobenzenetricarbonylchromium. The latter is a slow reaction ($k = 4.9 \times 10^{-5}$ sec$^{-1}$, under pseudo-first-order conditions at 64.9°), compared with our rates of alkaline hydrolysis, which is therefore the only observable process.

From the data of Tables III and IV it can be concluded that the chromium complexes react considerably faster than the corresponding uncomplexed aromatic compounds under comparable conditions. It is very interesting to note that the effect of the $Cr(CO)_3$ group on ester hydrolysis is almost exactly equal to that of a $p$-nitro group, as shown by the fact that the rate constants for the hydrolysis of $Cr(CO)_3C_6H_5COOCH_3$ and $p$-$NO_2C_6H_4COOCH_3$ are substantially the same. The equivalence in electron-withdrawing power between the chromium tricarbonyl and the $p$-nitro groups was also indicated by Nicholls and Whiting,[16] who measured the p$K$ values of $Cr(CO)_3C_6H_5COOH$ and $Cr(CO)_3C_6H_5CH_2COOH$.

The alkaline hydrolysis of both complexed and uncomplexed benzoic methyl esters is a bimolecular reaction of the SN2(lim) type.[17] For the chromium complexes, the intermediate of the reaction can therefore be represented as shown in Ib. The accelerating effect of the $Cr(CO)_3$ group on the rates of alkaline hydrolysis can be attributed to the fact that a higher positive charge on the reactive carbon will be created as a con-

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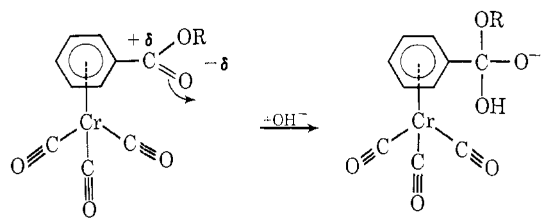

Ia Ib

sequence of the bonding to the central metal atom, thus favoring the approach of the incoming nucleophile.

The plots of log *k* for the alkaline hydrolysis of complexed and uncomplexed compounds *vs.* the known[18] Hammett $\sigma$ values are reported in Figure 1. The values of $\rho$ calculated from the slopes of the two plots are $+2.36$ for the hydrolysis of the uncomplexed esters and $+1.55$ for the hydrolysis of the chromium complexes. The value of $\rho$ for the uncomplexed esters compares well with that known from the literature[19] for the alkaline hydrolysis of ethyl benzoates ($\rho = +2.373$).

Of particular significance is the decrease in the value of $\rho$ for the hydrolysis of the chromium complexes with respect to the $\rho$ for the uncomplexed compounds. This means that the hydrolysis of complexed methyl esters is less sensitive to electronic changes in the aromatic ring induced by substituents. In other words, the lower value of $\rho$ for the chromium complexes suggests that the electronic changes on the electrophilic center are less important than in the case of the uncomplexed compounds. This also can be explained by the presence of the strongly electron-withdrawing chromium tricarbonyl group. In the parent compound, $Cr(CO)_3C_6H_5COOCH_3$, the aromatic system is largely deprived of $\pi$-electron density and the reactive carbon atom is strongly electrophilic. Further substitution to give $Cr(CO)_3RC_6H_4COOCH_3$ will therefore modify the situation on the ester carbon less than the same substituent will do in $RC_6H_4COOCH_3$. In actual fact, the decreased electron density on the aromatic ring bonded to $Cr(CO)_3$ will act against the removal of charge from the ring induced by substituents such as $COOCH_3$. On the other hand, the presence of bonded carbon monoxide groups with their well-known $\pi$-acceptor properties will considerably decrease the effect of $+R$ substituents such as $OCH_3$. The net result will be the observed lower value of the reaction constant $\rho$ (nonadditivity of Hammett's $\sigma$). The transmission of electronic effects induced by substituents from the aromatic ring to carbon monoxide groups has been directly established[20] by measurements of the infrared C–O stretching vibrations in the region 2000–1900 cm$^{-1}$ for a large series of substituted benzoic methyl ester–tricarbonylchromium compounds.

In Figure 2 log *k* values for the alkaline hydrolysis of uncomplexed benzoic methyl esters are plotted *vs.* log *k* values for the alkaline hydrolysis of complexed esters. The two sets of log *k* are linearly related for substituents in *meta* and *para* positions. No serious deviations from linearity are found except for the *p*-amino derivative. This can be due to experimental inaccuracy caused by the longer reaction time with consequent partial decomposition of the chromium complex. From the experimentally found linear re-

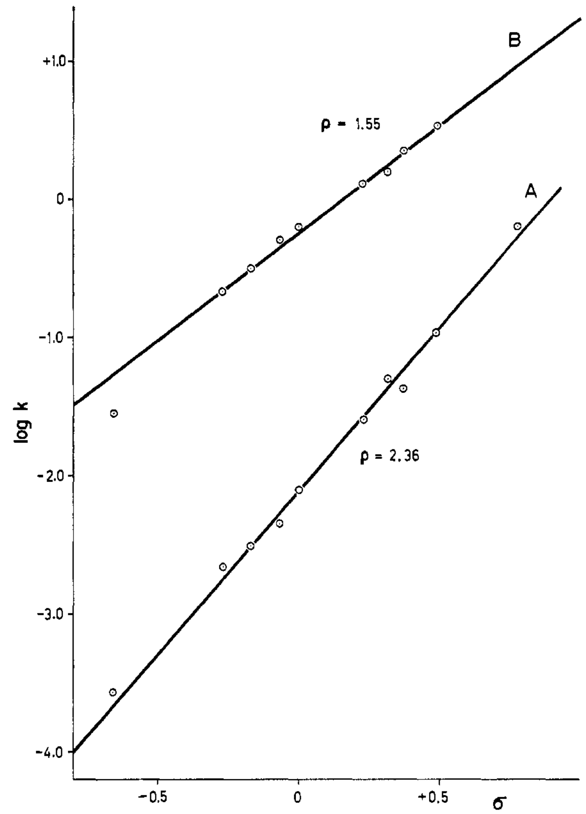

Figure 1.—Plot of log *k* against Hammett $\sigma$ constants. Points reading left to right: *p*-$NH_2$, *p*-$OCH_3$, *p*-$CH_3$, *m*-$CH_3$, H, *p*-Cl, *m*-$COOCH_3$, *m*-Cl, *p*-$COOCH_3$, *p*-$NO_2$. (A) Alkaline hydrolysis of substituted benzoic methyl esters. (B) Alkaline hydrolysis of substituted benzoic methyl ester–tricarbonylchromium compounds. The $\sigma$ value for *p*-$COOCH_3$ was obtained on plot A from the experimentally determined rate constant for the alkaline hydrolysis of *p*-$C_6H_4(COOCH_3)_2$ ($\sigma$ = 0.49).

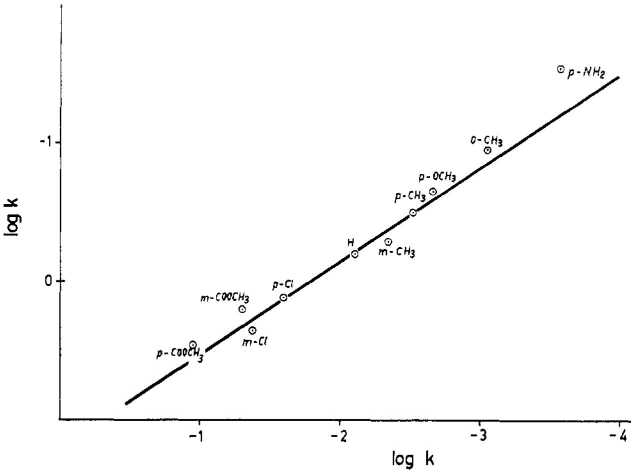

Figure 2.—Plot of log *k* for the alkaline hydrolysis of substituted benzoic methyl ester–tricarbonylchromium complexes *vs.* log *k* for the alkaline hydrolysis of substituted benzoic methyl esters.

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lationship between the two sets of alkaline hydrolysis comes the important conclusion that an aromatic system bonded to a $Cr(CO)_3$ group shows a dependence of reactivity on structure very similar to that of an uncomplexed aromatic system. This further supports the view of a completely delocalized type of bonding between the metal and the aromatic ring, in agreement with a recent X-ray determination of $Cr(CO)_3C_6H_6$, in which no significant deviations from a $D_{6h}$ symmetry of the hydrocarbon ligand were found to exist.[21]

Pettit and co-workers[10] have recently reported on the rates of solvolysis of (benzyl chloride)tricarbonylchromium. This appears to be an SN1 reaction with rate constants considerably higher than those of the corresponding uncomplexed compound. This was explained by an enhanced stability of the carbonium ion $Cr(CO)_3C_6H_5CH_2^+$ presumably formed in the rate-determining step; in turn the increased stability of the intermediate carbonium ion was attributed to back-feeding of electrons from the $Cr(CO)_3$ group into antibonding orbitals of the aromatic ligand.

Although the mechanism of benzoic ester–tricarbonylchromium hydrolysis is different from that of (benzyl chloride)tricarbonylchromium solvolysis, a similar stabilizing effect by the $Cr(CO)_3$ group on the incipient carbonium ion in I could be postulated in order to explain the observed increase of rate constants with respect to the uncomplexed compounds. That this explanation is incorrect in our case is shown by the fact that the $\rho$ of the chromium tricarbonyl complexes is positive; *i.e.* the reaction is accelerated by electron-withdrawing groups in *meta* and *para* positions. Negative values of $\rho$ would be observed if the stabilization of the incipient carbonium ion was the important factor.

We conclude by saying that the enhanced reactivity of complexed benzoic methyl esters can be best explained by a decreased electron density at the electrophilic center. Bond making appears to be the important factor in the alkaline hydrolysis of both the uncomplexed benzoic methyl esters and their chromium tricarbonyl complexes.

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# Organometallic Compounds with Metal–Metal Bonds. VII. Preparation and a Study of the Infrared Spectra of Mono- and Bis(tetracarbonylcobalt) Derivatives of Germanium and Tin[1]

BY D. J. PATMORE AND W. A. G. GRAHAM

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Infrared spectra in the carbonyl stretching region are reported and discussed for a large number of mono- and bis(tetracarbonylcobalt) derivatives of germanium and tin, most of which are new compounds. The monocobalt derivatives are of the types $X_nR_{3-n}GeCo(CO)_4$ ($X = Cl, Br, I$; $R = CH_3, C_6H_5$), $X_3SnCo(CO)_4$ ($X = Cl, I$), $R_3SnCo(CO)_4$ ($R = CH_3, C_6H_5$), and $(C_6H_5)_3PbCo(CO)_4$. Assignments are proposed for the three or four terminal stretching bands; a linear increase in frequency of the $A_1$ modes with electronegativity of substituents on germanium or tin is noted. The biscobalt derivatives are of the type $X_nR_{2-n}M[Co(CO)_4]_2$ ($M = Ge, Sn$), and two of the seven or eight observed carbonyl bands are tentatively assigned. Nmr spectra are reported for the methyltin derivatives. The compounds are moderately stable in the absence of air, and most are prepared by reaction of $Co(CO)_4^-$ with halides or organometallic halides of germanium or tin.

## Introduction

Compounds which would now be regarded as having tin–cobalt covalent bonds were first obtained in 1957.[2,3] Only analytical data were available for these compounds, and a satisfactory structural formulation was not then possible. It soon became evident that their general stability was much greater than that of simple organic derivatives such as $CH_3Co(CO)_4$, which decompose at temperatures above −35 to −20°.[4] There have been several more recent studies of compounds in which cobalt is bonded to tin,[5–8] as well as to silicon,[9–12] germanium,[6] and lead.[5]

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