# The Stereochemistry of Organometallic Compounds. Part XII.[1] The Acid Strengths of Some Tricarbonyl(alkylbenzoic acid)chromium Compounds, their Nuclear Magnetic Resonance Spectra, and the Spectra of Some Related Compounds

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The p$K_a$ values of a series of *m*- and *p*-alkylbenzoic acids and their related tricarbonylchromium compounds are reported. The influence of the alkyl groups on the p$K_a$ values and on the n.m.r. spectra of the acids, their sodium salts, and their methyl esters, and on the spectra of a related series of alkylanilines is discussed.

THE p$K_a$ values of a series of *m*- and *p*-substituted benzoic acids and their tricarbonylchromium compounds have been measured and are summarised in Table 1. The parent acids showed a decrease in acid strength with an increase in the inductive effect of the alkyl group; no Baker–Nathan effect was observed in this solvent system in contrast to p$K_a$ measurements in water.[5] Dewar[6] has suggested that solvation effects may well dominate small changes in p$K_a$ values and thus the different trends in the two solvent systems, although small, may be real.

The tricarbonyl(alkylbenzoic acid)chromium compounds were all stronger acids than the parent acids (*cf.* ref. 2) but the substituent effects now showed a different trend. Tricarbonyl-(*p*-t-butylbenzoic acid)-chromium was now the strongest *p*-substituted acid and tricarbonyl-(*p*-toluic acid)chromium the weakest. The increase in acid strength on forming a tricarbonylchromium complex was significantly less for the toluic acids (Δp$K_a$ 0·14 for the *meta*- and 0·35 for the *para*-acid) than for the other alkyl-substituted acids (Δp$K_a$ 0·63—0·90). This could be because the inductive effect of a methyl group is increased when attached to an electron-deficient ring because of its greater polarisability.[6]

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[4] J. D. Roberts, E. A. McElhill, and R. Armstrong, *J. Amer. Chem. Soc.*, 1949, **71**, 2923.

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TABLE 1

p$K_a$ Values for some alkylbenzoic acids and their tricarbonylchromium compounds

| Substituents | p$K_a$ * Parent ligand | Tricarbonylchromium compound | Δp$K_a$ |
|---|---|---|---|
| H | 5·70 [a] | 4·83 [c] | 0·87 |
| *p*-Me | 5·92 [b] | 5·57 | 0·35 |
| *p*-Et | 6·05 | 5·42 | 0·63 |
| *p*-Pr$^i$ | 6·05 | 5·36 | 0·69 |
| *p*-Bu$^t$ | 6·22 | 5·32 | 0·90 |
| *m*-Me | 5·88 | 5·74 | 0·14 |
| *m*-Pr$^i$ | 5·91 | 5·02 | 0·89 |

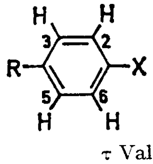
* ±0·03; Average of two or three determinations carried out at different dilutions in aqueous 50% methanol (v/v).

[a] Lit.,[2] 5·68; lit.,[3] 5·73. [b] Lit.,[4] 5·93. [c] Lit.,[2] 4·77.

Such enhanced polarisation should play an even more important role in determining the relative stabilities of a series of tricarbonyl(alkylanilinium)chromium cations. The base strengths of a series of tricarbonyl(*p*-alkylaniline)chromiums were therefore measured.

TABLE 2

N.m.r. spectra of 4-alkyl-1-substituted benzene derivatives and their tricarbonyl chormium spectra *

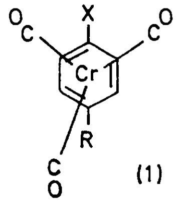


| X | R | τ Values for ring protons: Tricarbonylchromium compound 3- and 5-H | 2- and 6-H | $\Delta\tau_{(3,5-2,6)}$ | Free ligand 3- and 5-H | 2- and 6-H | $\Delta\tau_{(3,5-2,6)}$ |
|---|---|---|---|---|---|---|---|
| $NH_2$ | Me | 4·52 | 5·13 | −0·61 | 3·05 | 3·44 | −0·39 |
| | Et | 4·49 | 5·15 | −0·66 | 3·01 | 3·40 | −0·39 |
| | Pr$^i$ | 4·46 | 5·18 | −0·72 | 2·98 | 3·42 | −0·44 |
| | Bu$^t$ | 4·31 | 5·23 | −0·92 | 2·82 | 3·38 | −0·56 |
| $CO_2Me$ | Me | 4·88 | 3·83 | 1·05 | 2·69 | 2·06 | 0·63 |
| | Et | 4·87 | 3·85 | 1·02 | 2·72 | 2·02 | 0·70 |
| | Pr$^i$ | 4·81 | 3·88 | 0·93 | 2·71 | 2·01 | 0·70 |
| | Bu$^t$ | 4·58 | 3·98 | 0·60 | 2·55 | 2·01 | 0·54 |
| $CO_2H$ | Me | 4·88 | 3·79 | 1·09 | 2·72 | 1·99 | 0·73 |
| | Et | 4·87 | 3·79 | 1·08 | 2·70 | 1·93 | 0·77 |
| | Pr$^i$ | 4·82 | 3·83 | 0·99 | 2·70 | 1·95 | 0·75 |
| | Bu$^t$ | 4·59 | 3·88 | 0·71 | 2·52 | 1·95 | 0·57 |
| $CO_2^-Na^+$ † | Me | 4·46 | 3·78 | 0·68 | 2·70 | 2·18 | 0·52 |
| | Et | 4·45 | 3·86 | 0·59 | 2·70 | 2·10 | 0·60 |
| | Pr$^i$ | 4·37 | 3·91 | 0·46 | 2·70 | 2·05 | 0·65 |
| | Bu$^t$ | 4·09 | 3·86 | 0·23 | 2·53 | 1·97 | 0·56 |

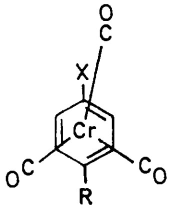
* Spectra were recorded for 5% solutions in $CDCl_3$ at 30° with tetramethylsilane as internal standard. † Spectra for 5% solutions in $D_2O$ containing sodium 3-(trimethylsilyl)propanesulphonate as internal standard.

Although all the amines were shown to be weak bases (p$K_a$ *ca.* 0·8), in agreement with a previous determination,[7] the experimental error was greater than the differences between the individual amines.

Previous work has shown that substituents of different sizes influence the preferred conformation of the tricarbonylchromium residue, as evidenced by n.m.r. spectra [8] and by the orientation of electrophilic acylation in complexed arenes.[9] Introduction of a methyl group leads to the preferred conformation (1) and of a t-butyl group to conformation (2) in the absence of directive effects from the group X.



(1)



(2)

*X*-Ray structural analyses of tricarbonyl-(*o*- and *m*-toluate)chromium anions have shown that in the solid state the carboxylate ion does not lead to a strong conformational preference for the tricarbonylchromium group.[10] Thus if conformational influences were important a *m*-methyl and a *p*-t-butyl group should influence the stability of the anion in a similar manner.

The changes in p$K_a$ on forming a metal complex are very different for *m*-toluic acid (Δp$K_a$ 0·14) and *p*-t-butylbenzoic acid (Δp$K_a$ 0·9), suggesting that the preferred conformation of the tricarbonylchromium group is not important.

In contrast, the n.m.r. spectra of the tricarbonyl(alkylbenzoic acid)chromium compounds, their sodium salts, and their methyl esters, and of a related series

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[7] E. O. Fischer, K. Ofele, H. Essler, W. Frohlich, J. P. Mortensen, and W. Semmlinger, *Chem. Ber.*, 1958, **91**, 2763.

[8] W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *J. Chem. Soc.* (*B*), 1969, 1214.

[9] W. R. Jackson and W. B. Jennings, *J. Chem. Soc.* (*B*), 1969, 1221.

[10] M. A. Bush, T. A. Dullforce, and G. A. Sim, *Chem. Comm.*, 1969, 1491.

of tricarbonyl(alkylaniline)chromium compounds can best be interpreted in terms of the conformational influence of the alkyl groups. The tricarbonylchromium residue prefers the conformation (1; $X = CO_2Me$ or $CO_2H$) when a strongly electron-withdrawing group is present.[11] This conformation is further stabilised by the presence of a *p*-methyl group. The presence of a *p*-t-butyl group destabilises the conformation (1; $X = CO_2Me$, $R = Bu^t$) relative to the alternative conformation (2; $X = CO_2Me$, $R = Bu^t$), thus leading to a decrease in the chemical shift separation, $\Delta\tau$, between the 2,6- and 3,5-protons. The converse situation applies to the aniline spectra and an intermediate situation in which neither conformation (1) nor (2) is strongly preferred exists for the sodium salts.*

TABLE 3

Tricarbonylchromium compounds of arenecarboxylic acids and their methyl esters

| Acid or ester | M.p. (°C) | Yield (%) | Found (%) C | Found (%) H | Formula | Required (%) C | Required (%) H |
|---|---|---|---|---|---|---|---|
| Methyl benzoate | 98—99<br>(lit.,[2] 97·5—98·5) | 67 | | | | | |
| Methyl *m*-toluate | 99—100<br>(lit.,[19] 101—102) | 25 | 50·6 | 3·75 | $C_{12}H_{10}CrO_5$ | 50·35 | 3·5 |
| Methyl *p*-toluate | 99—101<br>(lit.,[10] 104—105) | 63 | 50·65 | 3·7 | $C_{12}H_{10}CrO_5$ | 50·35 | 3·5 |
| Methyl *p*-ethylbenzoate | 73—74 | 89 | 52·3 | 4·3 | $C_{13}H_{12}CrO_5$ | 52·0 | 4·0 |
| Methyl *p*-isopropylbenzoate | 66—67 | 80 | 53·7 | 4·5 | $C_{14}H_{14}CrO_5$ | 53·5 | 4·5 |
| Methyl *m*-isopropylbenzoate | 67—68 | | 54·1 | 4·8 | $C_{14}H_{14}CrO_5$ | 53·5 | 4·5 |
| Methyl *p*-t-butylbenzoate | 64·5—66 | 27 | 55·5 | 5·3 | $C_{15}H_{16}CrO_5$ | 54·9 | 4·9 |
| Benzoic acid | 194—195 (decomp.)<br>[lit.,[2] 194 (decomp.)] | 97 | | | | | |
| *m*-Toluic acid | 150—155 (decomp.) | 87 | 48·4 | 3·2 | $C_{11}H_8CrO_5$ | 48·5 | 2·95 |
| *p*-Toluic acid | 149—150 (decomp.) | 73 | 48·3 | 3·15 | $C_{11}H_8CrO_5$ | 48·5 | 2·95 |
| *p*-Ethylbenzoic acid | 165—170 (decomp.) | 53 | 50·7 | 3·7 | $C_{12}H_{10}CrO_5$ | 50·35 | 3·5 |
| *p*-Isopropylbenzoic | 153—154 (decomp.) | 88 | 52·3 | 4·25 | $C_{13}H_{12}CrO_5$ | 52·0 | 4·0 |
| *m*-Isopropylbenzoic acid | 175—180 (decomp.) | 91 | 52·2 | 4·2 | $C_{13}H_{12}CrO_5$ | 52·0 | 4·0 |
| *p*-t-Butylbenzoic acid | 172—173 | 51 | 53·2 | 4·5 | $C_{14}H_{14}CrO_5$ | 53·5 | 4·5 |

TABLE 4

Tricarbonyl(arylamine)chromiums

| Amine | M.p. (°C) | Yield (%) | Found (%) C | Found (%) H | Found (%) N | Formula | Required (%) C | Required (%) H | Required (%) N |
|---|---|---|---|---|---|---|---|---|---|
| Aniline | 166—168 (decomp.)<br>[lit.,[2] 173—175 (decomp.)] | 30 | | | | | | | |
| *p*-Toluidine | 156—158<br>(lit.,[2] 156—157·5) | 41 | | | | | | | |
| *p*-Ethylaniline | 110·5—111 | 50 | 51·8 | 4·5 | 5·5 | $C_{11}H_{11}CrNO_3$ | 51·4 | 4·3 | 5·45 |
| *p*-Isopropylaniline | 146—147 | 35 | 53·5 | 4·8 | 5·05 | $C_{12}H_{13}CrNO_3$ | 53·15 | 4·8 | 5·2 |
| *p*-t-Butylaniline | 149—150 | 39 | 55·0 | 5·3 | 4·85 | $C_{13}H_{15}CrNO_3$ | 54·75 | 5·25 | 4·9 |
| *NN*-Dimethylaniline | 144—145<br>(lit.,[2] 145·8—146·5) | | | | | | | | |

## EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage. N.m.r. spectra were recorded by I. Jack and R. Spratt using a Varian HA100 spectrometer.

*Carboxylic Acids.*—The following arenecarboxylic acids were prepared by oxidation[12] of the appropriate acetophenones: *p*-toluic acid, m.p. 180—181° (lit.,[13] 180—182·5); *p*-ethylbenzoic acid, m.p. 112—113° (lit.,[14] 113·5); *p*-isopropylbenzoic acid, m.p. 117—118° (lit.,[15] 114—116); *p*-t-butylbenzoic acid, m.p. 164—165° (lit.,[16] 164); *m*-toluic acid, m.p. 110—111° (lit.,[17] 110—115); and *m*-isopropylbenzoic acid, m.p. 51—52° (lit.,[18] 51·2—51·8).

*Tricarbonyl(alkylbenzoic acid)chromiums.*—The above carboxylic acids were converted into their methyl esters. Hexacarbonylchromium was treated with an excess (3 mol. equiv.) of the ester under the conditions described by Nicholls and Whiting.[2] The esters were hydrolysed with aqueous methanolic sodium hydroxide solution and the complexed acids were recrystallised to constant m.p.

*Amines.*—Commercial samples were purified by standard methods. *p*-Isopropylaniline, b.p. 108° at 10 mmHg (lit.,[20] 222·5 at 760 mmHg) was prepared by the literature method.[20] *p*-t-Butylaniline had b.p. 76—78° at 1·5 mmHg, m.p. 14—15° (lit.,[21] m.p. 15—16°) when prepared by the method of Craig.[21]

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* For a more detailed discussion of the n.m.r. spectra see M. Ashraf, Ph.D. Thesis, Queen's University, Belfast.

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*Tricarbonyl(arylamine)chromiums.*—The arylamines were treated with hexacarbonylchromium in diglyme.[4]

*p*$K_a$ *Measurements.*—*Acids.* Solutions (0·005M) of the carboxylic acids in aqueous 50% ethanol (by volume) were prepared immediately before use. Portions (5 ml) were diluted (2 or 3 times) with aqueous 50% ethanol and titrated against standard 0·1N-sodium hydroxide solution under nitrogen using a Radiometer type S1001 automatic titrator with a combined glass/calomel electrode. The same stock of conductivity water and ethanol was used throughout these experiments. The pH scale on the titrator was checked before and after each experiment with a standard Radiometer Buffer (pH 6·50 ± 0·02). The p$K_a$ value for each acid was determined at two or three different dilutions and individual values are recorded below. The values for the corresponding tricarbonylchromium compound are given in parentheses: benzoic acid, 5·70, 5·70 (4·81, 4·85); *p*-toluic acid, 5·95, 5·90, 5·91 (5·54, 5·60, 5·58); *p*-ethylbenzoic acid, 6·05, 6·07, 6·06 (5·44, 5·40, 5·42); *p*-isopropylbenzoic acid, 6·04, 6·06, 6·06 (5·38, 5·34, 5·36); *p*-t-butylbenzoic acid, 6·24, 6·20 (5·32, 5·32); *m*-toluic acid 5·88, 5·88 (5·76, 5·72); *m*-isopropylbenzoic acid, 5·91, 5·90, 5·92 (5·02, 5·02). Average values are given in Table 1.

*Bases.* The spectroscopic method described by Eastes and Aldridge[22] was used. Acid solutions of tricarbonyl(alkylaniline)chromiums were found to be unstable, even when saturated with nitrogen, leading to large inaccuracies in p$K_a$ determination.

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