Journal of Organometallic Chemistry, 49 (1973) 219–225
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IONISATION AND APPEARANCE POTENTIAL MEASUREMENTS IN ARENE CHROMIUM TRICARBONYLS

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(Received June 29th, 1972)

SUMMARY

The ionisation potentials and the appearance potentials for ions arising from the loss of carbonyl groups as well as certain other low-energy fragmentation ions have been measured for a series of substituted arene chromium tricarbonyls. The values obtained are found to correlate very well, for the loss of one and two carbonyl groups, with both the C–O force constant k and the Hammett σ_p function of the substituent on the benzene ring. The appearance potentials of the ions arising by the loss of three carbonyl groups do not exhibit a high correlation. Arene$^+$ ions are found to occur at energies intermediate between those for the loss of two and three carbonyl groups.

The various effects observed are discussed in terms of a model which involves definite contributions from both σ- and π- bonding of carbonyl groups in the gaseous cations.

Although a considerable amount of work has been reported on the mass spectra of organometallic compounds[1], and several workers have studied ionisation potentials by this technique[2–10], only a small amount has been reported on the appearance potentials[11–19] of daughter ions.

In this paper we report on the ionisation potentials and some appearance potentials of compounds of the type $ArCr(CO)_3$ where Ar represents substituted benzene. The object of the work is to investigate the energetics of the fragmentation processes and to study the possibility of correlating the potentials with each other and with quantities such as the Hammett σ function of the substituents[20,21] on the benzene ring and the force constants of the carbonyl groups.

EXPERIMENTAL

All compounds studied were prepared by the method of Nicholls and Whiting[22] with the exception of benzene and toluene chromium tricarbonyls which were purchased commercially from Strem Chemicals Inc.

The mass spectra were measured with an AEI MS 12 instrument with an ionising potential of 50 eV, a trap current of 20 μA and an ion accelerating voltage of 8 kV. The samples were introduced into the mass spectrometer by means of a direct insertion

TABLE 1

IONISATION AND APPEARANCE POTENTIALS, DISSOCIATION ENERGIES, FORCE CONSTANTS AND INTERACTION CONSTANTS FOR THE SYSTEM X–ArCr-$(CO)_3$

Compound	*Parent(P) IP (eV)*	*P−1CO AP_1 (eV)*	*P−2CO AP_2 (eV)*	*P−3CO AP_3 (eV)*	*ArX AP (eV)*	*Cr^+ AP (eV)*	*Ligand IP (eV)*	*D_3 (eV)*	*D_2 (eV)*	*D_1 (eV)*	*$\bar{D}_3$ (eV)*	*$\bar{D}_2$ (eV)*	*σ_p*	*ν (cm. s^{-1})*	*ν_2 (cm. s^{-1})*	*k (mdyn/Å)*	*k′ (mdyn/Å)*
$(CH_3)_6C_6$-$Cr(CO)_3$	6.35	6.45	7.70	9.82	8.55	13.00		0.10	1.25	2.12	1.09	1.59	−1.02	1946.9	1866.8	14.485	0.411
$NH_2C_6H_5$-$Cr(CO)_3$	6.52	6.75	7.84	9.96	7.96	13.17	7.61	0.23	1.09	2.12	1.15	1.61	−0.62	1959.0	1875.9	14.640	0.429
1,3,5-$(CH_3)_3C_6$-$H_3Cr(CO)_3$	6.60	6.69	8.00	10.35	8.61	13.90	8.21	0.09	1.31	2.35	1.25	1.83	−0.51	1959.1	1880.4	14.686	0.407
o-$(CH_3)_2C_6$-$H_4Cr(CO)_3$	6.70	7.00	7.85	9.60	8.51	13.06	8.55	0.30	0.85	1.75	0.97	1.30	−0.34	1963.0	1882.3	14.726	0.418
$CH_3OC_6H_5$-$Cr(CO)_3$	6.75	6.95	7.90	9.90	8.45	12.65	8.25	0.20	0.95	2.00	1.05	1.48	−0.27	1967.4	1886.0	14.787	0.422
$CH_3C_6H_5$-$Cr(CO)_3$	6.69	7.09	8.11	10.04	8.31	13.42	8.80	0.40	1.02	1.93	1.12	1.48	−0.17	1967.6	1888.1	14.809	0.413
$C_6H_6Cr(CO)_3$	6.74	7.25	8.09	10.34	9.49	13.50	9.30	0.51	0.84	2.25	1.20	1.55	0	1971.2	1892.1	14.869	0.411
$CH_2OHC_6H_5$-$Cr(CO)_3$	6.92	7.32	8.19	10.35	9.40	14.01	9.00	0.40	0.87	2.16	1.14	1.51	+0.10	1971.0	1892.3	14.870	0.409
$ClC_6H_5Cr(CO)_3$	7.00	7.45	8.18	10.10	9.15	14.10	9.12	0.45	0.73	1.92	1.03	1.33	+0.23	1979.8	1905.5	15.052	0.389
$COOCH_3C_6H_5$-$Cr(CO)_3$	7.02	7.60	8.27	10.00	9.31	14.00	9.35	0.58	0.67	1.73	0.99	1.35	+1.32	1982.9	1910.8	15.123	0.378
Correlation coefficient with σ_p	0.976	0.986	0.930	0.378				0.886	0.870	0.383						0.976	—

probe at an ion chamber temperature of 120°. Ionisation and appearance potentials were determined using a semi-logarithmic method, employing helium, argon and krypton as standards and using a computer programme operating over the linear range of the ionisation efficiency curve to calculate the potentials at the $\bar{3}$-level[*].

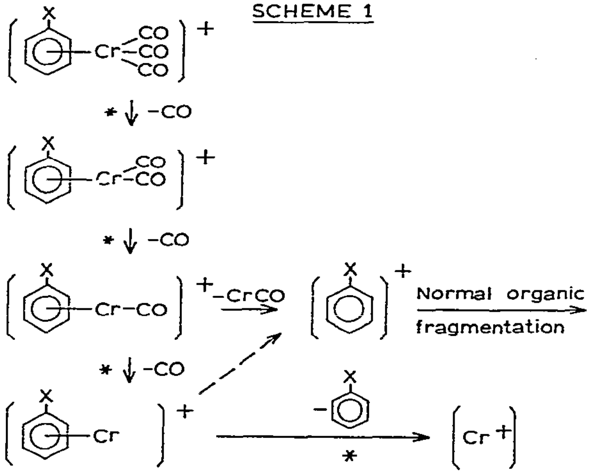
Infrared data were obtained using a Perkin–Elmer 225 instrument with dichloromethane as solvent.

DISCUSSION

All results are given in Table 1.

The ionisation potentials of the compounds vary with C–O force constants in a manner similar to that found by Müller[25], although our values are consistently lower. We believe this slight discrepancy reflects both the different instruments and calculation methods used. Variation with the Hammett σ_p function is similar, confirming that electron-withdrawing substituents tend to increase the ionisation potential. We agree with Müller's suggestion that the removed electron comes from an orbital derived largely from a metal 3*d* orbital involved in "back-bonding" to the carbonyl groups and to the arene ligand.

SCHEME 1



The occurrence of metastable peaks (indicated by an asterisk in Scheme 1) confirms that the principal fragmentation pathway at high electron energies (50 eV) is as shown in this scheme, *i.e.* stepwise loss of the three carbonyl groups followed by loss of the arene to give Cr^+. However the $Arene^+$ ions appear at energies below those of $ArCr^+$ and although we have not been able to observe metastable peaks for the process it is possible that $Arene^+$ can dissociate from all or any of the ions $ArCr(CO)_n^+$ where $n = 0–3$. As the appearance potentials of the arene ligands correlate well with the ionisation potentials of the free ligands it seems possible that $Arene^+$ can dissociate from the parent ion as soon as its own ionisation potential is exceeded. Thermal decomposition is discounted in the aforegoing since recent work[24] has established

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[*] An error of ±0.1 eV is considered reasonable in these values.

the compounds to be stable at temperatures up to 300°. We have not studied the internal fragmentation of Arene$^+$.

Figure 1 shows the correlation between the ionisation and appearance potentials for the loss of CO groups with the Hammett σ_p functions of the substituents. σ_p values for polysubstituted benzene ligands were taken as the sum of σ_p values for individual substituents[25]. The poor correlation of the appearance potential of ArCr$^+$ suggests that the characteristics of the substituents which make up σ_p (the electron withdrawing characteristics) do not constitute the only factors influencing the loss of the last CO group. No specific factor has been found to account for this, but the most likely possibility seems to be "competitive shift" caused by the production of Ar$^+$ at lower energies.

If the assumption is made that the ions ArM(CO)$_2^+$, ArM(CO)$^+$ and ArM$^+$

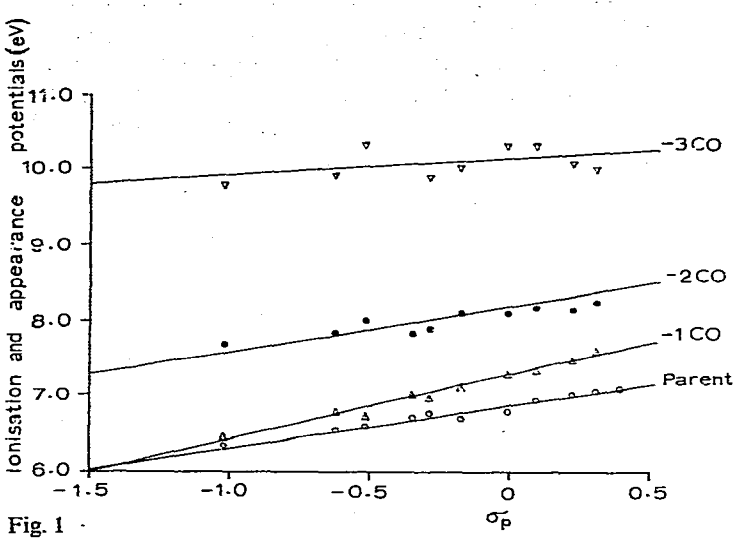

Fig. 1

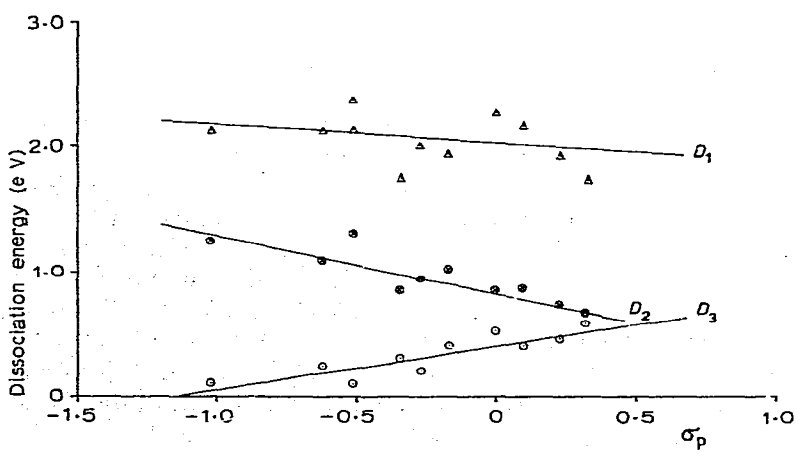

Fig. 2

are produced by simple fission of the metal–carbon bonds, without rearrangement occurring, then it is possible to suppose that the back reactions have negligible activation energies particularly since they involve only the formation of coordinate bonds. Under these circumstances, the differences between successive appearance potentials are equal to the stepwise dissociation energies of the carbonyl groups.

We define the energy D_i to be the energy required to dissociate a carbonyl group from the ion $ArM(CO)_i^+$. Figure 2 shows that D_3 ($D_3 = AP_1 - IP$) increases with σ_p and the C–O force constant, k, whereas D_2 and D_1 decrease. It is also found that for all compounds $D_1 > D_2 > D_3$.

In the chemistry of metal carbonyl derivatives it is usually found that electron-withdrawing ligands tend to weaken the bonding of carbonyl groups to the metal atom and this is generally interpreted as being due to the weakening of the ability of the metal to back-donate electrons into the π^* orbitals of the carbonyl groups. The decrease of D_2 and D_1 (insofar as the latter is significant) and the increase of the ionisation potential of the parent molecule with σ_p and k are consistent with this picture, but the increase of D_3 with σ_p requires further discussion.

The ability of an electron-withdrawing ligand (positive σ_p) to cause a secondary ligand to be more tightly bound to the metal atom must be associated with an increasing tendency of the metal atom to draw charge from the secondary ligand. The most likely source of such charge in a carbonyl group is the lone pair on the carbon atom. It should be noted that in a mass spectrometer isolated cations are under examination; there is no mechanism, as there would be in solution, for the positive charge to be dispersed over a fairly large volume by solvation. It might therefore be expected that the effects of oxidation on a carbonyl derivative would be much more noticeable than they are in solution. For these reasons we believe that the σ-bonding, or forward donation of electrons, and its variations are of much greater importance in the chemistry of gas-phase cations than they are in condensed phases. Any interpretation of the dissociation energies must then include a consideration of $C \rightarrow M$ σ-bonding as well as π-bonding considerations.

There are three facts obtainable from the data which appear to be significant:

(*a*), the dissociation energy of the carbonyl from the ions $ArCr(CO)_i^+$ falls with increasing i;

(*b*), the pattern of this fall-off seems to depend on the substituent of the arene;

(*c*), the slopes of D_3 and D_2 against σ_p are positive and negative respectively.

The value of the slope of D_1 *vs.* σ_p is uncertain but the most probable value is small and negative.

There are two general effects which might influence the behaviour of D_i as a function of i. The metal atom presumably has a limited capacity to bond carbonyl groups and, in the absence of concerted mutual bonding effects, it would be expected that the larger the number of carbonyl groups the smaller the share of bonding capacity of the metal would be otained by each carbonyl group. It might also be expected that carbonyl groups would repel each other and hence the larger the number the lower the dissociation energy.

The bonding of a particular carbonyl group to a metal atom may be divided into σ and π components, and repulsion from other carbonyls treated as a third component. As stated previously, σ-bonding would be expected to increase with σ_p, and π-bonding to decrease; the existence of a positive slope of D_3 *vs.* σ_p is sufficient to indicate the importance of σ bonding.

The experimental data are not accurate enough (particularly D_1 values) to afford a quantitative interpretation, but the following scheme affords some qualitative ideas. If we restrict discussion at this point to the behaviour of D_3 and D_2 only, it can be concluded that, since $D_2 > D_3$ in all cases, the two mechanisms of bond-sharing and inter-carbonyl repulsion are operative although the relative amounts of each cannot be estimated.

The opposite slopes of D_3 and D_2 *vs.* σ_p suggest strongly that σ- and π-bonding are involved significantly but to different extents in dicarbonyls and tricarbonyls. As D_3 is relatively small neither type of bonding can be large in an absolute sense, but the positive slope for D_3 suggests that σ-bonding may be the more important contribution. Both σ- and π-bonding may contribute more to the larger values of D_2, but the negative slope in this case indicates that the π-component has become relatively much larger than in the case of D_3. One plausible argument in favour of such a phenomenon is that in a dicarbonyl of C_{2v} symmetry all possible linear combinations of carbonyl π^* orbitals belong to representations which also contain metal *d*-orbitals, whereas in a tricarbonyl of C_{3v} symmetry the A_2 combination of π^* orbitals cannot overlap with any metal *d*-orbitals. Thus the π-bonding situation is *more efficient* for the dicarbonyl, exactly how much more efficient depending on the inter-carbonyl angles in the two cases.

The most probable slope of D_1 *vs.* σ_p is small and negative; if this situation is correctly assessed, then the argument above suggests a loss of π-bonding efficiency in a monocarbonyl, as only two metal *d*-orbitals (in C_{6v} symmetry) are available to the carbonyl π^* orbitals. However this conclusion is very tentative as the slope of D_1 is subject to a large error, and the π-bonding can be changed by distortion from C_{6v} symmetry.

It can be argued that a dissociation energy D_i contains a term for rearrangement of the product (those rearrangements with high kinetic energy release can be excluded since metastable peaks are in all cases narrow in width); for example on dissociating $ArCr(CO)_3^+$ to $ArCr(CO)_2^+$ there are almost certainly minor rearrangements such as change of intercarbonyl angle. Such effects may be allowed for by using average stepwise dissociation constants defined as $\bar{D}_i$ by the equation

$$\bar{D}_i = \frac{1}{i}\sum_{j=1}^{j=i} D_j$$

In our experiments, the quantities $\bar{D}_i$ have a fairly large error attached to them because of the error in D_1. Nevertheless it is found that $\bar{D}_3 < \bar{D}_2 < \bar{D}_1$ in all cases, thereby lending further support to the conclusions about bond-sharing and inter-carbonyl repulsion. The slopes of $\bar{D}_i$ *vs.* σ_p however, do not appear to be particularly significant, but it is not possible to state whether this is due to the randomness of D_1 or to other causes.

ACKNOWLEDGEMENT

We are grateful to the Science Research Council for an equipment grant to JRM.

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