

ALTERATION OF REACTIVITY OF ARENES IN THE MASS SPECTROMETER BY π COMPLEXATION TO CHROMIUM.

SCRAMBLING OF DEUTERIUM IN COMPLEXED STYRENE

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The alteration of reactivity of organic ions in the mass spectrometer by their complexation to transition metals¹ has indicated in earlier studies that the structures typically proposed as a result of scrambling studies on organic ions are not always achieved when an organic fragment of the same composition is bonded to a transition metal. The C_7H_7 fragment bonded to iron does not completely achieve a symmetrical structure;² C_4Ar_4 bonded to iron appears to assume a cyclobutadiene structure, rather than a completely scrambled structure, before it fragments;³ and toluene and cycloheptatriene do not achieve similar structures before they decompose further,⁴ as they do when they are ionized directly.

Labeling studies of the mass spectral fragmentation of styrene show that randomization of deuterium is nearly complete before all fragmentations of the molecular ion, and can be interpreted as isomerization of the carbon skeleton to a cyclooctatetraene form.⁵ The spectra of cyclooctatetraene and styrene are similar and support such an interpretation.⁶

We report here that the scrambling of deuterium in α -deuterostyrene differs from the reported nearly complete scrambling when it is complexed with chromium; that is, labeling results for a fragmentation of $C_8H_8Cr^+$ differ from those for $C_8H_8^{++}$. We restrict our discussion here to the accurate mass spectra in the region of the ions formed by loss from $C_8H_8Cr^+$ and $C_8H_8^{++}$ of various C_2 fragments, which show essentially complete scrambling in the case of styrene itself.⁵

α -Deuterostyrene was prepared in two steps. Acetophenone was reduced by $LiAlD_4$ to 1-phenyl-

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ethanol-1-d in 80% yield.⁷ Subsequent dehydration using a modification of the method of Bernstein *et al.*⁸ afforded an 82% yield of α -deuterostyrene, bp 60°/40 mm. α -Deuterostyrene-tricarbonyl-chromium* was obtained in 45% yield by a procedure similar to that used for the synthesis of styrene-tricarbonyl-chromium.⁹ Low-voltage mass spectrometric analysis showed this compound, and therefore its precursor, to be >99% d-1. Samples of styrene and α -deuterostyrene were introduced through the heated inlet system of a Hitachi RMU-6E mass spectrometer at 180°; the respective tricarbonyl-chromium complexes were introduced by a direct probe at ambient temperature into an unheated source (α . 50°). Spectra obtained on different days showed satisfactory reproducibility (α . 5% of relative intensity for small (5-10%) peaks, *i.e.*, 0.3-0.5% overall).

Our spectra of styrene and α -deuterostyrene were nearly identical to those of Quinn and Mohler, and our spectra of the metal complexes were analyzed by their method.⁵ The data in Table I illustrate our finding that the spectra calculated for complete scrambling of the label in

Table I. Scrambling of the D Label in C_6 Ions in the Mass Spectrum
of α -Deuterostyrene-tricarbonyl-chromium†

m/e	rel inten in $C_8H_8Cr(CO)_3$			rel inten in $C_8H_7DCr(CO)_3$				
	observed	corr'd for ^{13}C	rescaled base=104	calcd*	scaled x 0.67	rescaled base=105	corr'd for ^{13}C	observed
80			→	3	2	3	←	3
79	8	→	3	→	32	30	←	29
78	66	→	61	→	53	37	←	36
77	57	→	56	→	27	21	←	20
76	11	→	10	→	9	5	←	5
75	9	→	8	→	8	5	←	5
74	10	→	10	→	8	4	←	4

$C_8H_8^{+}$ predict the general distribution observed in the deuterated compound rather well (*cf.* columns 6 and 7). The total intensity of the cluster of peaks (74 to 80) in the deuterated compound was less than the total intensity of the cluster in the parent compound by a factor of 0.67. Column 6 reflects a correction for this general lowering of intensity.

*Found: C, 54.78; H+D, 3.70. Calcd for $C_{11}H_7CrDO_3$: C, 54.78; H+D, 3.76. Nmr ($CDCl_3$): apparent triplet (1 H), τ 4.33 (vinylic proton *cis* to phenyl); multiplet (6 H, centered at τ 4.59 (phenyl protons and vinyl proton *trans* to phenyl).

†Calculated by method of ref 5.

Table II shows a similar calculation for the ion intensities in the region corresponding to the C_6Cr ions on the assumption of complete scrambling. The data suggest that this time complete

Table II. Scrambling of the D Label in C_6Cr Ions in the Mass Spectrum
of α -Deuterostyrene-tricarbonyl-chromium

m/e	rel inten in $C_8H_8Cr(CO)_3$			rel inten in $C_8H_7DCr(CO)_3$			
	observed corrd for isotopes			calcd	corrd for isotopes	observed	
132				1	1	←	1
131	2	→	1	1	1	←	3
130	7	→	1	16	15	←	15
129	26	→	26	11	6	←	6
128	2	→	2	2	1	←	1
127	4	→	2	1	1	←	1

equilibration is not achieved, since the calculated amount of m/e 129 is nearly twice that observed, a disparity which cannot be concealed by application of a scaling parameter: even though the total intensity of the ion cluster in the deuterated compound is again lower than the intensity of the cluster in the standard compound, no scaling will alter the ratio of the intensities at m/e 129 and 130. The former is far too low to correspond to complete scrambling; a route for decomposition exists for the production of $C_6H_5Cr^+$ before scrambling of hydrogen is complete.

Our data therefore indicate two important observations: (1) although the amount of $C_8H_8^{++}$ fragmenting to C_6 ions differs for the $C_8H_8^{++}$ produced by fragmentation of the metal complex (Table I) and that produced directly from styrene (Table 1, ref 5, gives only 38% for m/e 78 in styrene) both $C_8H_8^{++}$ exhibit essentially complete scrambling of H before these reactions. Scrambling must be fast relative to the rates of fragmentation, then, because ions with sufficiently different internal energies to produce quite different amounts of fragments are both completely scrambled. Mechanisms of scrambling and mechanisms of fragmentation must be distinct processes with different time scales. (2) Again, the metal atom alters the structure(s) of $C_8H_8Cr^+$ ions, since randomization of H in the ligand is noticeably different from randomization in $C_8H_8^{++}$ before these ions decompose to $C_6H_5Cr^+$ and $C_6H_5^+$, respectively.

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