

Specificity in the Homogeneous Metal-catalysed Isotopic Hydrogen Exchange of Polycyclic Aromatic Hydrocarbons. Evidence for Complex Formation Between Aromatic Hydrocarbons and Transition Metals

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RECENTLY we reported¹ that aromatic compounds exchange *homogeneously* with isotopic water in the presence of Pt^{II} and Pt^{IV} salts. It is now found that useful specificity of isotope is obtained with the polycyclic aromatic hydrocarbons under these conditions. The results (Tables 1 and 2) also

indicate that complexes (presumably of a π -complex type) are readily formed between the polycyclic hydrocarbons and Pt^{II}. When compared with *heterogeneous* exchange on platinum,^{2,3} the most active of the pre-reduced Group VIII transition metals, the present *homogeneous* procedure is

TABLE 1

Initial rates of homogeneous metal-catalysed exchange of polycyclic aromatics at low temperature^a

Compound	Weight (g.)	Reaction time (min.)	% D ^b	Distribution									
				D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈	
Benzene	0.088	135	7.81	87.8	1.65	1.65	1.85	2.05	2.40	2.70			
Biphenyl	0.100	135	4.98	83.0	3.0	4.0	5.5	1.7	1.3	1.5			
Bibenzyl	0.100	135	3.10	83.5	3.8	4.6	5.5	1.1	0.7	0.5	0.30	0.1	
<i>o</i> -Terphenyl ..	0.100	135	4.47	80.4	3.9	4.5	3.9	2.4	1.8	1.4	0.1	0.4	
<i>m</i> -Terphenyl ..	0.100	135	3.87	80.4	4.6	4.5	6.0	2.2	1.1	0.8	0.5		
Naphthalene ..	0.100	135	3.62	75.3	20.4	3.3	0.6	0.06					
Phenanthrene ..	0.100	50	2.00	80.7	16.2	1.4	0.25						
Benzene	0.088	40	2.83	95.5	0.59	0.62	0.71	0.74	0.83	0.98			
Pyrene	0.050	40	1.57	85.4	13.7	1.0							

^a Reaction conditions involved Na₂PtCl₄ (0.02 M) in CH₃-CO₂D (66.7 mole % in D₂O) at 75° (note no HCl used); 2.5 ml. portions for each run.

^b Calculated from the observed distribution for all hydrogens in the molecule.

TABLE 2

Homogeneous metal-catalysed exchange of polycyclic aromatics at 100°^a

Compound	Weight (g.)	% D ^c	% D (theoretical)	Experimental distribution									
				D ₀	D ₁	D ₂	D ₃	D ₄	D ₅	D ₆	D ₇	D ₈	D ₉
Benzene	0.33	45.2	75.5	22.2	10.4	12.2	14.7	17.3	15.5	7.5			
Biphenyl	0.110	41.0	91.5	3.3	4.4	8.5	16.6	20.0	25.4	21.9			
Biphenylmethane	0.135	32.3	88.7	4.9	5.1	9.8	19.1	18.8	21.8	16.6	2.0	0.5	0.2
Bibenzyl	0.130	27.5	88.5	5.8	10.7	11.5	13.4	16.5	18.4	16.5	4.6	2.3	0.4
<i>trans</i> -Stilbene ..	0.095	9.3	92.0	31.8	36.8	22.0	7.3	1.9	0.2				
<i>o</i> -Terphenyl ..	0.160	34.2	88.8	3.1	4.2	8.2	11.3	14.7	17.0	17.4	15.2	8.8	0.1
<i>m</i> -Terphenyl ..	0.110	34.7	92.3	1.2	2.5	6.1	11.0	16.5	21.2	24.7	17.0	0.0	
<i>p</i> -Terphenyl ^b ..	0.065	3.33	95.4	88.6	1.1	1.2	1.5	2.0	2.4	3.1	0.0		
Naphthalene ..	0.105	36.1	95.8	0.8	6.2	19.1	37.8	31.1	4.9	0.3			
Pyrene	0.100	22.5	93.8	8.6	10.3	42.6	27.7	8.4	2.1	0.4			
Phenanthrene ..	0.105	33.9	93.3	0.1	1.9	13.2	36.6	41.9	5.4	1.0			
Anthracene ^b ..	0.035	29.25	97.8	38.5	0.9	1.7	5.6	17.9	22.3	12.2	2.7	0.3	
Chrysene ^b ..	0.022	3.4	98.3	89.5	0.1	1.1	2.3	4.7	1.0	1.3			

^a Reaction conditions involved CH₃-CO₂D (67 mole % in D₂O) containing HCl (0.02 M) and Na₂PtCl₄ (0.02 M), heated at 100° for 5 hr.; 2.4 ml. portions used in each run.

^b Organic compounds not completely dissolved under experimental conditions.

^c Calculated from the observed distribution for all hydrogens in the molecule.

much faster and more efficient for the isotopic hydrogen labelling of the above series.

A significant feature of the data (Tables 1 and 2) is the remarkable orientation effects observed in these compounds, with n.m.r. confirming the trends indicated from the cut-offs in the low-voltage mass spectra. Diphenyl and the terphenyls exchange only in the sterically unhindered *meta*- and *para*-positions (Figure) even at 100°. As methylene

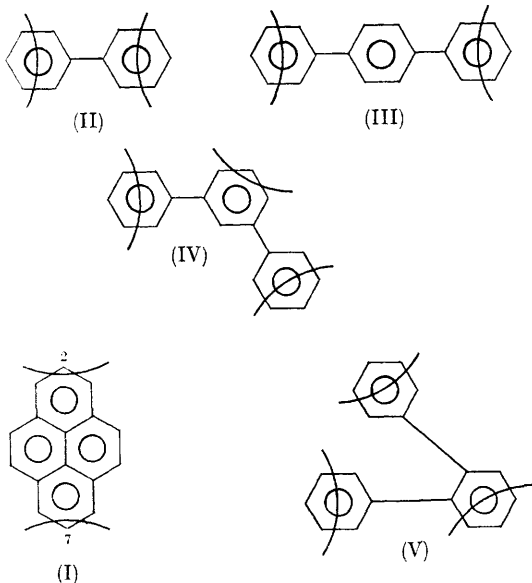
groups are inserted between the phenyl groups (biphenyl \rightarrow dibenzyl), the degree of isotope incorporation is progressively reduced. At 75°, naphthalene, anthracene, phenanthrene, and chrysenes exchange almost exclusively in the β -positions. As the temperature is increased, deuteration progressively increases so that ultimately at 130°, complete exchange occurs in all positions. With pyrene, initial deuteration is observed selectively in the 2,7-positions (species I) at 75° where reactions were performed without HCl. At 100° (Table 2), however, some HCl (0.02 M) is necessary, as originally reported,¹ to prevent precipitation of platinum.

The orientation of isotope in the condensed ring aromatics, particularly naphthalene, indicates that the concept of bond order is important in the mechanism of the exchange at 75°, and that, initially, a π -olefin type complex is probably formed with platinum(II). From extensive data,⁴ this step would appear to be followed by a π - σ conversion to give a Pt-C σ -bonded intermediate.

In addition to the importance of the present work in fundamental catalysis, the method is ideal as a preparative tritium-labelling tool and is to be preferred to both *heterogeneous* catalysis^{2,3} and radiation-induced methods⁵ for the tritiation of compounds discussed in the attached Tables.

The authors thank the Australian Research Grants Committee and the donors of the Petroleum Research Fund of the American Chemical Society for financial support.

(Received, September 29th, 1967; Com. 1037.)



FIGURE

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