1270. *The Kinetics of the Reaction between Arenes and Hexacarbonylmolybdenum*

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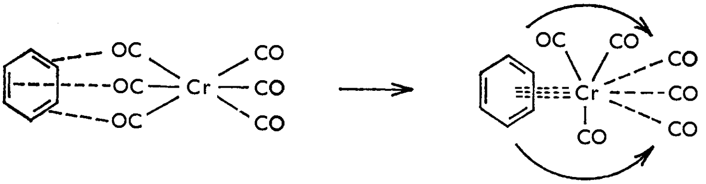
It is shown that the reaction between mesitylene, and benzene, and hexacarbonylmolybdenum is first-order with respect to metal carbonyl, in accord with the proposed inversion mechanism and in contrast to the previously reported kinetics of the reaction between *p*-xylene and hexacarbonylmolybdenum.

It has been suggested[1] that the reaction of arenes and hexacarbonylmetals of Group VIB to form the tricarbonylarenemetals[1-3] proceeds by an S_N2 Walden inversion type mechanism with expulsion of the three carbonyl groups on the side of the metal atom opposite to that of the approaching arene, followed by inversion of the other carbonyl groups. The reaction should then be first-order in both arene and metal carbonyl.



Strohmeier[4] reported a comparative study of the reaction of substituted benzenes and hexacarbonylmolybdenum in terms of the carbon monoxide evolved in a closed system; electron-donating substituents accelerated the reaction. Strohmeier *et al.*[5] observed the following rate law for the reaction of *p*-xylene and hexacarbonylmolybdenum in n-heptane–n-decane solvent mixtures, again following the reaction by the carbon monoxide evolved:

$$\text{Rate} = k[\text{Arene}]^{\frac{1}{3}}[\text{Mo(CO)}_6]^{\frac{1}{2}}$$

This expression is obviously incompatible with the S_N2 mechanism. Independently, we have measured the kinetics of the reaction between mesitylene, and benzene, and hexacarbonylmolybdenum. Identical experiments involving hexacarbonylchromium were abandoned because of sublimation of carbonyl at the temperatures at which reaction proceeds measurably (~100°). Even in the case of hexacarbonylmolybdenum, attempts to follow the reaction by means of the carbon monoxide evolved in a rapid stream (220 ml. min.$^{-1}$) of pure nitrogen caused up to 30% loss of carbonyl; accordingly, the reaction was followed spectrophotometrically.

The reaction solvent was refluxing 2,2,4-trimethylpentane, but despite careful deoxygenation it was only possible to follow the reaction up to about 40%, after which side-decomposition of the complex became important. Ratios of [Arene] to [Mo(CO)_6] between 10 : 1 and 100 : 1 were also found necessary to give measurable rates.

Under these conditions, the reaction between mesitylene and hexacarbonylmolybdenum was first-order in metal carbonyl concentration (Tables 1 and 2). The reaction with benzene gave identical kinetics although the error in rate constant is greater because of the lower rate and slightly lower reaction temperature. It should be noted that the results in Table 1 confirm Strohmeier's observation of the accelerating effect of electron-donating substituents.

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

[2] B. Nicholls and M. C. Whiting, *J.*, 1959, 551.

[3] G. Natta, R. Ercoli, and F. Calderazzo, *Chimica e Industria*, 1958, **40**, 287.

[4] W. Strohmeier, *Chem. Ber.*, 1961, **94**, 3337.

[5] W. Strohmeier, Afaf El-Said Mahgoub, and D. von Hobe, *Z. phys. Chem.* (*Frankfurt*), 1962, **35**, 253.

We suggest that the method due to Strohmeier and his co-workers does not ensure complete removal of carbon monoxide; indeed, these authors concluded that the concentration of dissolved carbon monoxide varied during reaction, which is in agreement with our observation that rate determinations based on evolved carbon monoxide are dependent on the flow rate of the carrier gas. In contrast, in the spectrophotometric method the rate was independent of flow rate in the range in which no loss of carbonyl occurred. However, with zero flow rate the spectrophotometric rate was low and deviation from first-order kinetics occurred (run 1, Table 1).

TABLE 1

All kinetic runs were carried out using a 100-fold molar excess of the arene

Run	Flow of N_2 (ml. min.$^{-1}$)	10^3[Mo(CO)$_6$] (moles l.$^{-1}$)	Reaction temp. (°c)	Arene	$10^6 k_1$ (sec.$^{-1}$)
1	0	6·03	100·0	Mesitylene	2·5 *
2	20	6·00	100·0	Mesitylene	4·2
3	60	6·41	100·0	Mesitylene	4·8
4	30	5·96	100·0	Mesitylene	4·4
5	30	6·09	100·0	Mesitylene	4·6
				$k_{av.}$ =	4·5
6	25	6·30	97·0	Benzene	1·1
7	25	6·05	96·0	Benzene	1·0
8	20	5·86	96·0	Benzene	1·1
				$k_{av.}$ =	1·1

* The rate constant for run 1 was obtained from the slope of the " best " straight line from the graph of log [Mo(CO)$_6$]$_t$ against t. There was a deviation from linearity for this run.

TABLE 2

Run no. 3

Time (min.)	Optical density λ_{290}	λ_{322}	10^3 [Mo(CO)$_6$] (moles l.$^{-1}$)	$10^6 k_1$ (sec.$^{-1}$)
0	0·470	0·070	6·41	—
210	0·444	0·076	6·02	4·98
420	0·424	0·088	5·69	4·72
480	0·422	0·096	5·63	4·47
1380	0·324	0·105	4·21	5·08
1440	0·325	0·111	4·20	4·88
			Average	4·83

Mo(CO)$_6$ $\varepsilon_{290} = 1{\cdot}81 \times 10^4$, $\varepsilon_{322} = 2{\cdot}50 \times 10^3$; π-Mesitylene Mo(CO)$_3$ $\varepsilon_{290} = 5{\cdot}23 \times 10^3$, $\varepsilon_{322} = 2{\cdot}01 \times 10^4$.

Our kinetic studies are in agreement with the mechanism proposed by Fischer *et al.*,[1] in contrast to those of Strohmeier *et al.*,[5] and the latter authors' conclusion that the above mechanism requires revision is not, in our opinion, correct.

Note added in proof.—Since submission of this Paper, we have learnt from Dr. H. Werner, Inorganic Chemistry Laboratory, Technische Hochschule, München, that he has made similar studies to our own. The general conclusions are similar and again first-order kinetics in metal carbonyl concentration are observed(H. Werner and R. Prinz, *J. Organometallic Chem.*).

EXPERIMENTAL

Spectra were measured on a Unicam S.P. 500 spectrophotometer. Solvent and reactants were dried and deoxygenated according to standard methods. Hexacarbonylmolybdenum was sublimed three times before use.

Kinetic Experiments.—The reaction flask (250 ml.) contained a gas inlet tube, thermometer well, condenser, and self-sealing sampling device. The volume of solvent was maintained by means of a pre-saturator which, together with the reaction vessel, was kept in an oil thermostat. All runs were carried out under pure nitrogen. The arene (*ca.* 0·1 mole) and solvent (150 ml.) were deoxygenated in the reaction vessel, and, after cooling the system, hexacarbonylmolybdenum (*ca.* 0·001 mole) was added; equilibrium was attained rapidly. Sampling was by means of a 1-ml. hypodermic syringe, and dilutions of 1 : 25 were employed.

The concentrations of the hexacarbonylmolybdenum and the tricarbonylarenemolybdenums were calculated using independently obtained molar extinction coefficients. The rate constants were calculated algebraically from the hexacarbonylmolybdenum concentrations.

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