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AUTOXIDATION OF CHROMIUM AND MOLYBDENUM ARENE COMPLEXES

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SUMMARY

The kinetics and the products of the autoxidation of dibenzenechromium, bis(ethylbenzene)chromium, ethylbenzene(diethylbenzene)chromium and ethylbenzene(diethylbenzene)molybdenum in various hydrocarbons have been investigated. The interaction of the above organometallic compounds with oxygen may be represented as a bimolecular reaction. It has been established that the reaction is catalysed by a number of ligands.

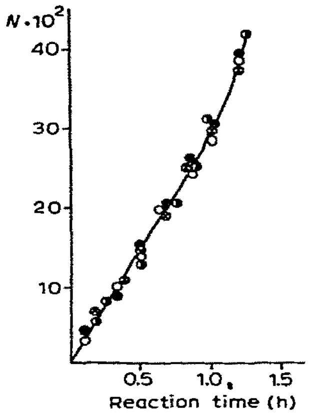
To date the autoxidation of arene complexes of transition metals has been very little studied. In this work, studies have been made of the mechanism of the autoxidation of dibenzenechromium, bis(ethylbenzene)chromium, ethylbenzene(diethylbenzene)chromium and ethylbenzene(diethylbenzene)molybdenum in various hydrocarbon solvents. It has been suggested[1] that autoxidation of chromium arene complexes proceeds only in the presence of water; our studies indicate otherwise.

We have shown that the autoxidation by carefully dried oxygen of the abovementioned arene complexes in hydrocarbon solvents proceeds readily even at room temperature, and that addition of water causes an increase in the reaction rate. Similarly, addition of various compounds with electrondonor properties causes positive kinetic effects in the autoxidation process.

A study of the kinetics of the autoxidation of dibenzenechromium, bis(ethylbenzene)chromium and ethylbenzene(diethylbenzene)chromium in the absence of water indicates that the process is first order with respect to the concentration of the organochromium compound and first order with respect to oxygen. This is shown by inspection of the reaction curves obtained at different initial concentrations (C_0) of organometallic compound by plotting N, where N is the number of moles of oxygen absorbed per mole of dibenzenechromium, against time (Fig. 1), and secondly by the observation that the rate of the reaction is proportional to the pressure of oxygen over the reaction mixture (Fig. 2).

From the use of radical inhibitors, it has been established that the autoxidation of organochromium compounds does not proceed by a free-radical mechanism, nor do such processes play a significant role in the reaction (Fig. 3).

Autoxidation of ethylbenzene(diethylbenzene)molybdenum proceeds readily even at −70°, and it has been established that the kinetic characteristics of this



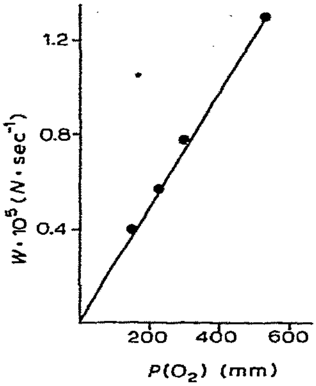


Fig. 1. Oxidation of dibenzenechromium in p-xylene at a temperature of 40° and a pressure of 300 mmHg; 10^2 $C_0 = 1.44$, 2.36, 3.5 and 4.6 mol·l^{-1} respectively.

Fig. 2. Dependence of the rate (W) of oxidation of dibenzenechromium in p-xlee ($T40°$, $C_0 = 2.36 \times 10^{-2}$ mol·l^{-1}) on the pressure of oxygen above the reaction mixture.

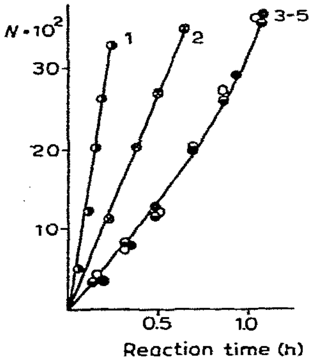


Fig. 3. Oxidation of dibenzenechromium in p-xylene at a temperature of 40° and a pressure of 300 mmHg; $C_0 = 2.36 \times 10^{-2}$ mol·l^{-1}.

Curves 1–5 were obtained in the presence of the following additives (n being the content of additive in moles per mole of starting organometallic compound):

1 = 2,6-di-tert-butyl-4-methylphenol, $n = 2.5 \times 10^{-1}$;
2 = galvinoxyl, $n = 2.5 \times 10^{-1}$;
3 = diphenylamine, $n = 1 \times 10^{-2}$;
4 = o-phenylenediamine, $n = 1 \times 10^{-2}$;
5 = no additive.

process are very similar to those established for chromium arene complexes. The results obtained enable the autoxidation of chromium and molybdenum arene complexes to be formally represented as bimolecular heterolytic reactions.

We have also investigated the products of the autoxidation of chromium and molybdenum arene complex[2–4]. It has been observed that the autoxidation of dibenzenechromium, ethylbenzene(diethylbenzene)chromium, and ethylbenzene(diethylbenzene)molybdenum is characterised by the liberation of ligand and the formation of solid products to which the formulae $[(C_6H_6)_2Cr]_2CrO_4$ (precipitate A) and $MoO_{2.88}$ may be assigned, respectively. Precipitate A is unstable and may be oxidized further with the formation of additional quantities of ligand, changing during this process to the final solid product of composition $5Cr_2O_4 \cdot 2C_6H_6$ (precipitate B).

In case of bis(ethylbenzene)chromium and ethylbenzene(diethylbenzene)-chromium, in addition to the liberation of the corresponding ligands and the formation of precipitates similar to A and B, acetophenone may also be detected amongst the reaction products in yields of 7 and 4%, respectively, of that theoretically possible. It is possible that the acetophenone is formed as a result of the oxidation of the liberated ethylbenzene, but ancilliary experiments have shown that oxidation of ethylbenzene does not occur during the autoxidation of bis(ethylbenzene)chromium and ethylbenzene(diethylbenzene)chromium.

During the reaction of the organometallic compounds with oxygen, formation of the intermediate complex $Ar_2M{-}O_2$ seems to be accompanied by the liberation of ligand, and in some cases by the oxidation of it.

The influence of temperature on the autoxidation of chromium arene complexes has been also studied in this work. The values of apparent activation energies for the autoxidation of dibenzenechromium, bis(ethylbenzene)chromium and ethylbenzene(diethylbenzene)chromium have been determined as 22, 20.9 and 21.2 $kcal \cdot mol^{-1}$, respectively.

EXPERIMENTAL

Chromium and molybdenum arene complexes were prepared by the method previously reported[5] and purified by fractional and molecular distillation to yield a main product of 95–99.9% purity. Other chromium and molybdenum arene derivatives were detected as impurities. Solvents of the "chemical pure" type used in the work (heptane, decane and xylene) were purified before use by the usual method[6]. Oxygen was obtained by the decomposition of "chemical pure" type potassium permanganate and dried before use by consecutive treatment over molecular sieves followed by circulation through a trap cooled with liquid nitrogen over a period of 40–50 min. Oxidations were undertaken using a circular vacuum apparatus, the experimental procedure being identical to that described earlier[7]. Liquid reaction products were analysed by elemental analysis, through the quantity of oxygen absorbed, or ESR and IR spectroscopy.

REFERENCES

1 B. G. Gribov, D. D. Mozzhukhin et al., *Dokl. Akad. Nauk SSSR*, 196 (1971) 586.
2 V. M. Fomin, Yu. A. Alexandrov, V. A. Umilin and V. Ya. Bordzilovsky, *Dokl. Akad Nauk SSSR*, in press.
3 V. M. Fomin, Yu. A. Alexandrov, V. A. Umilin and S. A. Lebedev, *Zh. Obschch. Khim.*, in press.
4 V. M. Fomin, Yu. A. Alexandrov, V. A. Umilin and T. A. Kondratyeva, *Zh. Obshch. Khim.*, in press.
5 E. O. Fischer and W. Hafner, *Z. Naturforsch. B*, 10 (1955) 665.
6 A. Weissberger, E. S. Proskauer, J. A. Riddick and E. E. Toops, Jr, "Organicheskiye rastvoritely", Izd-vo "IL"., Moscow, 1958.
7 G. A. Razuvaev, Yu. A. Alexandrov, V. N. Glushakova and N. G. Figurova, *J. Organometal. Chem.*, 14 (1968) 339.