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Catalytic Reactions of Anisole and Deuterium on Metal Films

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The reactions between anisole and deuterium have been followed over films of nickel, platinum, or palladium using a mass spectrometer to determine the products. No exchange occurs in the methoxy group except at high temperatures over nickel. The side group appears to have little directing influence on ring exchange except on nickel where the hydrogen atoms in the *ortho* positions are replaced more slowly than the other ring hydrogens.

There are some similarities between the reactions of anisole and the behavior of alkylbenzenes on the metal films. Thus, exchange is faster than the deuteration to form cyclohexyl methyl ether over nickel but both reactions occur at comparable rates on platinum and palladium. Some hydrogenolysis involving the rupture of the phenyl–oxygen bond occurs on platinum and the slow deuteration on nickel is also accompanied by hydrogenolysis of anisole.

INTRODUCTION

The catalytic exchange of organic molecules with deuterium has provided valuable information on the reaction mechanisms and on the intermediate surface compounds involved in catalysis. As larger and more complicated molecules were investigated, it became difficult to interpret some of the data from the exchange reactions solely in terms of σ-bonded intermediates and recently, the concept of π-bonded intermediates has proved useful (*1–5*).

The present paper reports a study of exchange and other reactions of anisole with deuterium on evaporated films of nickel, palladium, and platinum. Anisole is an interesting molecule for study as it has four types of hydrogen atoms that may exchange at different rates. The presence of the methoxy group may lead to some differences in the exchange behavior of anisole in comparison with alkylbenzenes. Finally, there is the possibility that the molecule may undergo hydrogenation or hydrogenolysis concurrently with exchange. The object of this investigation was to determine the relative rates of exchange of the various types of hydrogen atoms and the nature of the other reactions of anisole with deuterium as a function of the metal.

Exchange reactions of anisole and heavy water have been studied. Garnett and Sollich (*6*) observed 30% exchange in anisole after reaction on an Adams' platinum catalyst for 71 hr at room temperature, the ring hydrogen atoms exchanging more rapidly than those in the methyl group. Ueda and Hirota (*7*) treated anisole with D_2O for 150 hr at 100°C over various catalysts. Only ring exchange was observed on nickel (from nickel formate) but both the ring and the methyl group were exchanged on nickel-on-alumina and on palladium black. In acid-catalyzed reactions in solution, the three ring hydrogen atoms in the *ortho* and *para* positions of anisole are exchanged readily (*8, 9*).

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The literature on the catalytic hydrogenation and hydrogenolysis of anisole up to 1956 has been reviewed by Smith (*10*) who concluded that if the C–O bonds were broken during the reaction, the bond adjacent to the ring was usually attacked to a greater extent. On platinum oxide (*11*) and platinum-rhodium oxides (*12*) at room temperature, the main hydrogenation product was cyclohexyl methyl ether (CHME). More than 80% of this compound was also found at 160° on nickel-on-alumina (*12*) and on ruthenium oxide at 80°C (*13*).

No results appear to be available on the exchange of anisole with deuterium (as opposed to D_2O) but pertinent data on the exchange of alkylbenzenes on nickel films have been reported (*3*). Whan and Kemball (*14*) have studied the hydrogenolysis of diethyl ether on platinum films.

EXPERIMENTAL

The apparatus and the technique for evaporating the wires have been described previously (*15, 16, 17*). The essential feature of the apparatus was the connection of the reaction vessel (198 ml) to a Metropolitan-Vickers MS2 mass spectrometer by a capillary leak and, in this way, continuous analyses could be made of the reaction mixture throughout the course of the reaction. Films were evaporated with the walls of the reaction vessel at 0°C.

The anisole was Laboratory Reagent grade from British Drug Houses, Ltd. It was stored over sodium chips for several days and then examined by gas chromatography, which revealed no impurities. The standard reaction mixture consisted of 0.82 torr of anisole with a 20:1 ratio of deuterium:anisole; this mixture was admitted to the reaction vessel at 0°C and so the vessel contained 5.9×10^{18} molecules of anisole. Rates were measured at a series of temperature with nickel films up to 175°C but with palladium and platinum, the anisole had reacted completely after periods of about 30 min at 75° and 25°C, respectively.

Mass spectrometric analyses were made with an ionizing beam of 25-V electrons which gave adequate sensitivity without excessive fragmentation. After correcting for the presence of naturally occurring heavy carbon and deuterium, the mass spectrum of anisole, shown in Table 1, was similar to that reported by Meyer and Harrison (*18*) for 50-V electrons except for an expected reduced sensitivity in the peaks for *m/e* of 92 and 93. These authors demonstrated that no rearrangement occurred in the type of fragmentation involving the loss of the methyl group from anisole-methoxy-d_3. Thus, we were able to determine the isotopic content of the ring hydrogen atoms from peaks in the range from 93 to 98 as well as the isotopic content of the complete molecules from the parent ions.

TABLE 1
MASS SPECTRUM OF ANISOLE WITH 25-V ELECTRONS

m/e	108	107	93	92
Abundance of ion after correction for naturally occurring isotopes	100	2.37	13	1.17

No attempt was made to analyze the mass spectra of CHME as neither an authentic sample nor a mass spectrum was available. However, from the kinetic data it was established that the ratio of the heights of the uncorrected peaks of CHME in the range from 114 upwards to the corrected peaks for the parent ions of anisole from which the CHME was formed was 34:100. Once CHME was formed it was no longer possible to use the peaks from 93 to 98 to provide data on the isotopic content of the ring in anisole because fragment ions from CHME appeared in this range.

In some experiments the reaction products were removed for analysis by NMR or gas chromatography. The reaction was stopped by surrounding the reactor with liquid nitrogen and evacuating the deuterium-hydrogen mixture. The condensable compounds were then distilled to a collection tube in liquid nitrogen by warming the reactor to 0°C. For NMR analyses, carried out on a Varian HR-100 spectrometer, the combined products from two or three successive experiments on the same film were collected and dissolved in carbon tetrachloride. The activity of the catalyst was substantially lower in the second and third experiments. Samples for chromatographic analysis were dissolved in *n*-pentane and a Pye-Argon unit was used with a 4-ft silicone oil column operated at 25°, 50°, 75°, or 100°C. The system was calibrated with known samples of anisole, benzene, cyclohexane, methanol, and phenol.

RESULTS

The methods used to interpret the rate data from the exchange reaction have been described (*19*). Three parameters were measured for the exchange reactions: k_0, the initial rate of disappearance of the light compound expressed as a percentage of the total anisole present; k_ϕ, the initial rate of entry of deuterium into 100 molecules of anisole and finally $M = k_\phi / k_0$, the average number of deuterium atoms entering each anisole molecule which reacted initially.

Initial rates of hydrogenation or hydrogenolysis of anisole k_H were obtained from the decrease in the total concentration of anisole with time which was found to follow reasonably good first-order plots.

Overall Course of the Reactions

Data obtained at 0° and 25°C for the rates of exchange and of the reaction of anisole in two experiments on each metal are given in Table 2. It may be seen that nickel is the most effective catalyst for exchange but relatively ineffective in deuterating or decomposing the molecule. Platinum has a lower activity for exchange than nickel but it shows the greatest activity for the other reactions. Palladium has the lowest activity for exchange and the rates of the other reactions are about equal to those for exchange.

TABLE 2
INITIAL RATES OF EXCHANGE AND REACTION OF ANISOLE

	Temp. (°C)	Ni	Pt	Pd
Exchange, k_0	0	40, 92	4.5, 15	0.16[a]
(% min^{-1} 10 mg^{-1})	25	—	24, 71	0.94[a]
Decrease in anisole, k_H	0	~0	0.7, 2.5	0.26[a]
(% min^{-1} 10 mg^{-1})	25	0.78, 0.43	2.8, 22	0.45, 0.46

[a] Identical values for two experiments.

The Exchange Reactions

Figure 1 shows the course of the exchange of anisole on a nickel film at temperatures of 0°, 25°, and 50°C. No isotopic species containing more than five deuterium atoms were formed in this temperature range and by examining the fragment ion peaks from 93 to 98 it was found that all the exchange was occurring on the aromatic ring. The average deuterium content of the molecules based on the peaks 93 to 98 was within ±3% of the average deuterium content based on the parent ions from 108 to 113. The exchange reaction over palladium (Fig. 2) and platinum was also limited to the replacement of five hydrogen atoms and by analogy with the results on nickel it was assumed that only the ring hydrogen atoms were reacting; too much cyclohexyl methyl ether was formed over these metals to permit the use of peaks 93 to 98 as a check on this assumption.

Some initial distributions of the isotopic species formed by the exchange reaction are shown in Table 3 together with values of M derived from them and also from the ratio k_ϕ / k_0. Stepwise or simple exchange occurs on palladium and platinum and even on nickel the extent of the multiple exchange is small since M was only 1.3.

We now examine the question as to whether all the five ring hydrogen atoms in anisole exchange at the same rate or

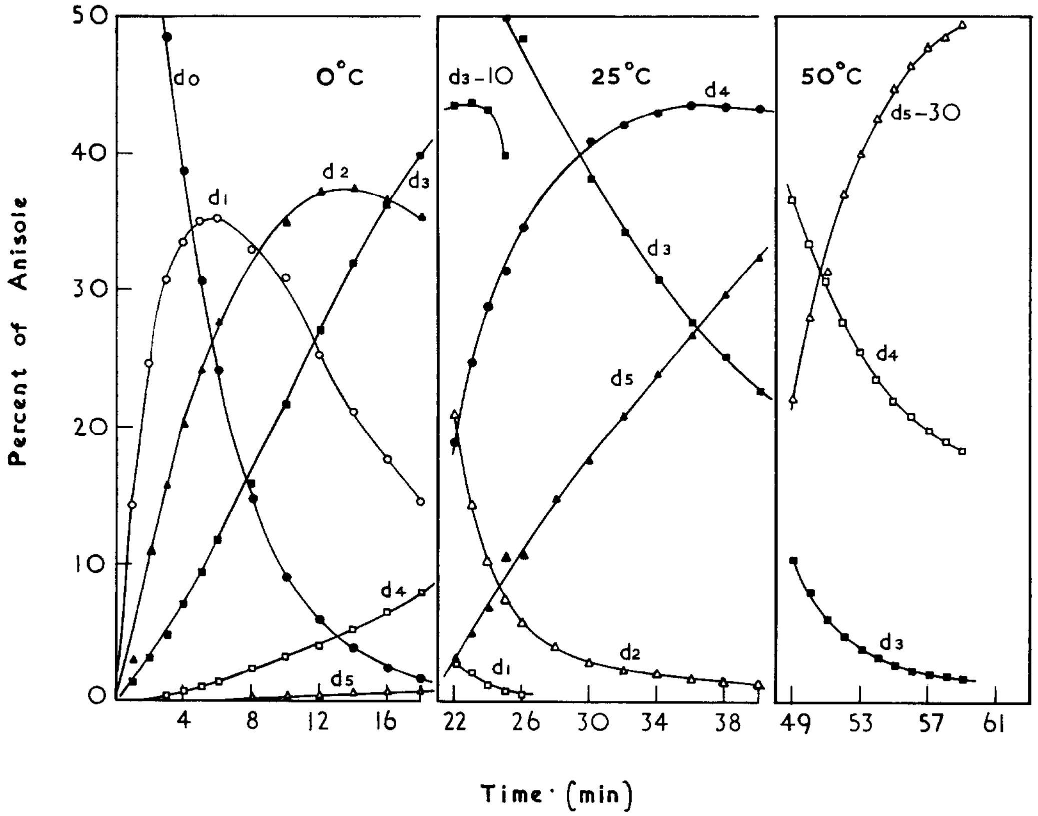

FIG. 1. The exchange of anisole with deuterium on a nickel film at 0°, 25°, and 50°C successively.

TABLE 3

INITIAL DISTRIBUTIONS OF PRODUCTS FROM THE EXCHANGE OF ANISOLE

Catalyst	Temp. (°C)	d_1	d_2	d_3	M from distributions	M (k_ϕ/k_0)
Ni	0	69.4	25.0	5.6	1.36	1.27
Pt	0	94.2	3.1	2.7	1.09	1.09
Pd	0 & 25	100	0	0	1.00	1.00 1.02

whether there is some difference in the reactivity of the atoms in the *ortho*, *meta*, or *para* positions. Some evidence on this problem may be obtained from a comparison of the experimental distributions of products at different stages of the exchange with calculated sets assuming a random distribution of the deuterium atoms over the five positions in the ring. Provided that the amount of multiple exchange is small, the occurrence of a random or binomial distribution of isotopic molecules *during* an exchange reaction may be taken as evidence for equal rates of exchange of all the hydrogen atoms under consideration (*19*). The data, shown in Table 4, indicate that the experimental distributions on platinum agree closely with the calculated binomial distributions and those for palladium are also similar. On the other hand, with nickel there is a marked divergence from the binomial pattern such that the observed values of d_3 are higher and those of d_4 and d_5 lower than the calculated values. So we can say, to a first approximation, that all five ring hydrogen atoms are replaced at the same rate on platinum and probably palladium but that over nickel three positions give a faster reaction than the remaining two. The differences between the patterns of the distributions in Fig. 2 with a regular buildup of the isotopic species on palladium and the results in Fig.

1 for nickel with a gap between d_3 and d_4 provide supporting evidence for these conclusions.

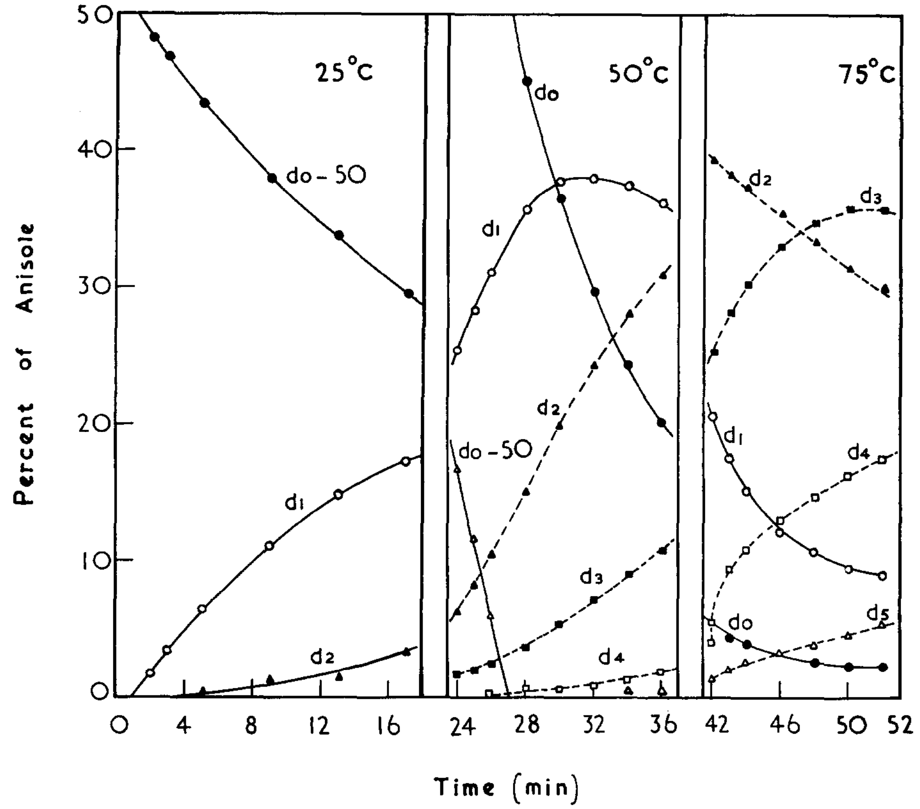

FIG. 2. The exchange of anisole with deuterium on a palladium film at 25°, 50°, and 75°C successively.

TABLE 4
PRODUCTS DURING EXCHANGE OF ANISOLE

Catalyst	Temp. (°C)	ϕ	d_0	d_1	d_2	d_3	d_4	d_5
Ni	0	97.6	38.7	33.5	20.1	7.0	0.7	0
Pt	25	98.2	34.6	39.5	19.6	5.8	0.5	0
Pd	50	96.1	36.5	37.7	19.8	5.3	0.6	0.1
Calculated		100	33.0	40.9	20.4	5.1	0.6	0
Ni	0	199.6	5.9	25.3	37.1	27.2	4.1	0.5
Pt	25	204.6	8.0	24.4	33.4	24.5	8.8	0.9
Pd	75	213.2	5.6	20.7	39.3	25.2	7.8	1.4
Calculated		200	8.0	25.8	34.5	23.0	7.7	1.0
Ni	25	297.3	0.6	2.8	20.8	53.5	19.0	3.3
Pt	25	295.0	1.7	8.9	22.4	33.9	25.4	7.7
Pd	75	304.2	1.9	7.9	20.2	35.4	24.3	10.3
Calculated		300	1.1	7.7	23.0	34.6	25.9	7.7

Attempts were made to gain some quantitative information about the rates of exchange of the different hydrogen atoms on the ring of anisole. The quantity k_ϕ has been defined already and it is determined from the equation

$$-\log_{10}(\phi_\infty - \phi) = k_\phi t/2.303\phi_\infty - \log_{10} \phi_\infty \quad (1)$$

where $\phi = \Sigma i d_i$, d_i being the percentage of the anisole present containing i deuterium atoms at time t and ϕ_∞ is the equilibrium value. We now define two further quantities

$$\phi_{2+} = \frac{d_2 + 2d_3 + 3d_4 + 4d_5}{d_1 + d_2 + d_3 + d_4 + d_5} \quad (2)$$

and

$$\phi_{4+} = \frac{d_4 + 2d_5}{d_3 + d_4 + d_5} \quad (3)$$

which we use in equations analogous to Eq. (1) to determine k_{2+} and k_{4+}. The first of these measures the further exchange of species which already contain one deuterium atom and the second measures the rate of exchange in the fourth and fifth positions of the ring of molecules which already contain three deuterium atoms. Now for a catalyst over which all five ring hydrogen atoms are equally easily exchanged we should expect to find the ratios $k_{4+}:k_{2+}:k_\phi$ to be given by 2:4:5. Some experimental ratios of k_{2+}/k_ϕ and k_{4+}/k_ϕ for the three metals are given in Table 5. Although the methods of determining the various rates are approximate, some useful trends can be noted. The ratios are closest to the expected values for platinum for which we have already had good evidence that the rates of exchange of all five ring hydrogen atoms are equal. The biggest departure from "ideal behavior" is the ratio of k_{4+}/k_ϕ on nickel, confirming that two ring positions react much more slowly (perhaps by a factor of 10 to 20) than the first three ring positions. Also since k_{2+}/k_ϕ is lower on nickel than on platinum there is some support for a grouping of the hydrogen atoms as $1 > 2 \gg 2$ in terms of rate of exchange on nickel. The results with palladium are intermediate between those for nickel and platinum but are closer to platinum than to nickel.

TABLE 5
RATIOS OF RATES OF EXCHANGE OF ANISOLE

Catalyst	Temp. (°C)	k_{2+}/k_ϕ	k_{4+}/k_ϕ
Pt	25	0.66	0.28
Pd	50	0.43	0.12
Ni	0	0.26	0.015
Expected if all 5H react at same rate		0.80	0.40

Use was made of NMR analysis of anisole which had been exchanged over nickel at 0°C to an average content of 2.22 deuterium atoms in order to establish which ring hydrogen atoms were more easily replaced. The NMR spectrum of anisole contains three readily separable groups of peaks: the first for the *meta*, the second for the *ortho* and *para*, and the third for the methyl hydrogen atoms. From the NMR data the ratio of the decrease of the area for the hydrogen atoms in the *ortho* and *para* positions to the decrease of the hydrogen atoms in the *meta* position was computed assuming that the area under the methyl peak corresponded to three hydrogen atoms. An absolute comparison between the loss of hydrogen determined by NMR and the mass spectral data could not be made because the exchanged sample was contaminated with light anisole as it was recovered through the inlet train to the reaction vessel. The experimental ratio is given in Table 6 together with ratios calculated from the mass spectral analyses on the following alternative assumptions:

TABLE 6
NMR DATA ON EXCHANGED ANISOLE FROM NICKEL AT 0°C

Ratio of loss of hydrogen atoms		Δ(*ortho* + *para*)/ Δ(*meta*)
Observed		0.60 ± 0.06
Calculated	(a) $p > m > o$	0.86
(see text)	(b) $p = m > o$	0.59
	(c) $p = o > m$	16.6
	(d) $p = m = o$	1.50

(a) all deutero species include *para* exchange, the additional deuteriums in d_2 and

d_3 correspond to *meta* and the extra in d_4 and d_5 to ortho exchange;

(b) d_1 to d_3 correspond to *para* and *meta* exchange with equal probability in all three positions and the additional atoms in d_4 and d_5 correspond to *ortho* exchange;

(c) d_1 to d_3 correspond to *ortho* and *para* exchange with equal probability in all three positions and the additional atoms in d_4 and d_5 correspond to *meta* exchange;

(d) exchange occurs equally easily in all ring positions.

The experimental ratio agrees most closely with case (b) but the results are not sufficiently accurate to exclude the possibility that the *para* hydrogen atom is replaced slightly more readily than those in the *meta* positions, which would correspond to a calculated ratio between those for cases (a) and (b).

Some data on the influence of the partial pressure of deuterium on the rate of exchange on nickel films at 0°C are reported in Table 7. The rate of exchange increased with the pressure of deuterium to about the 1.5 power.

TABLE 7

EFFECT OF DEUTERIUM PRESSURE ON EXCHANGE ON NICKEL AT 0°C

Partial pressure, D_2 (torr)	4.1	16.4	24.2
Ratio D_2:anisole	4.7	20.0	29.5
Rate of exchange, k_0 (% min^{-1} 10 mg Ni^{-1})	6.3	40	98

A slow exchange producing the d_6 and higher isotopic species was observed over nickel films at 150° and 175°C and the rate of disappearance of the d_5 compound was 1.3 and 1.5% min^{-1} 10 mg Ni^{-1}, respectively, at these temperatures. No exchange beyond the d_5 compound was observed over platinum or palladium because of the removal of anisole by other reactions at comparatively low temperatures.

Reactions Other Than Exchange

Over the temperature range 0° to 75°C with palladium, there was an increase of the total uncorrected peaks for cyclohexyl methyl ether which was proportional to the decrease in the peaks corresponding to the parent ions of anisole. Some typical results are shown in Fig. 3 and the slope of the lines for palladium corresponded to

$$-100\Delta \text{ anisole} \equiv 34\Delta \text{ CHME}$$

We have assumed that this constant value of the slope, also found for platinum at 0°C, corresponded to conversion of anisole to the cyclohexyl methyl ether, and this value has been used as an internal calibration for the sensitivity of the ether in the mass spectrometer.

On platinum at 25°C, see Fig. 3, less CHME was formed per unit of anisole reacted than at 0°C and it appeared that only 80% to 90% of the anisole consumed was converted to CHME. When the anisole had all reacted at 25°C the products were removed and examined by means of gas chromatography. A large peak was observed for CHME, smaller peaks for benzene, cyclohexane, and methanol, but no phenol, cyclohexanol, or anisole was detected.

On nickel films only about half of the anisole disappearing was converted to CHME but the reactions removing anisole were slow compared with exchange. In a total time of 60 min over the sequence of temperatures 0°, 25°, and 50°C, when the average deuterium content had reached 4.8, only about 30% of the anisole had reacted.

A complete analysis of the extent of exchange which occurred during or subsequent to the deuteration of anisole to CHME could not be made but the maxima in the peaks for CHME were compared with the maxima in the anisole peaks. Some care is required in interpreting these data as the isotopic content of the CHME is an integral quantity showing the deuterium content of the molecules produced from the start of the experiment; however, in the present tests conducted with a sequence of increasing temperatures most of the CHME was formed in the last part of the test. If no exchange occurs during deuteration which, therefore, involves merely the addition of six atoms, we expect to find the maximum in the CHME peaks occurring at not more than 12 mass units

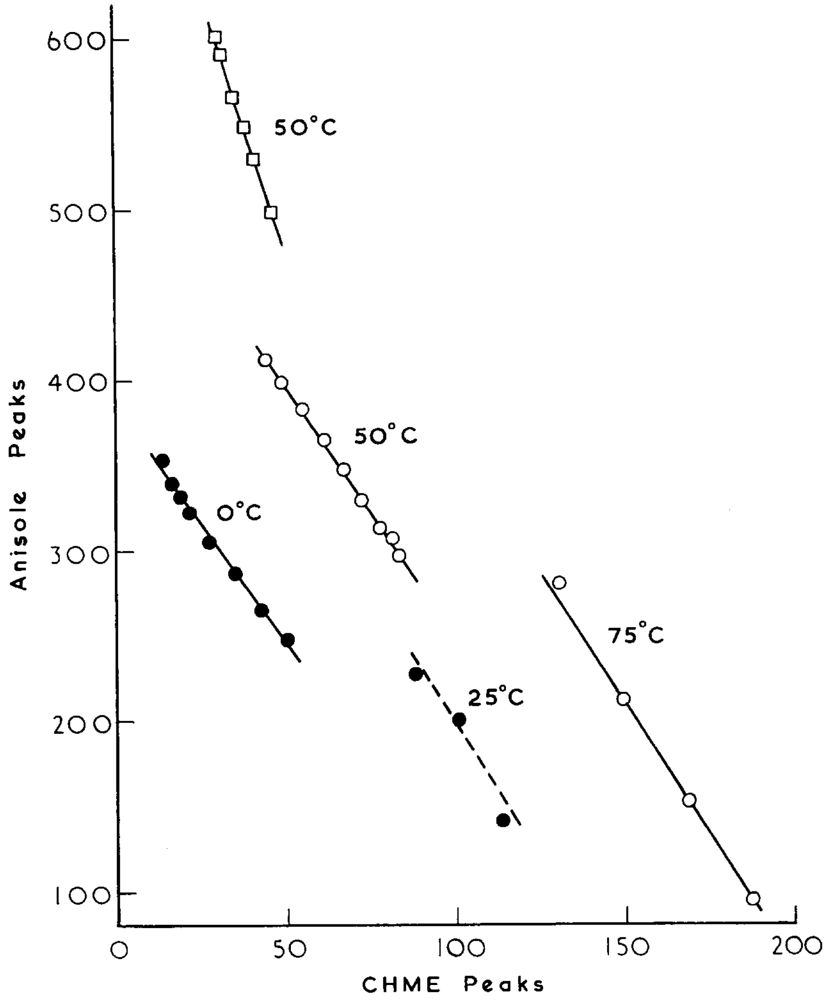

FIG. 3. Plots of the total corrected peaks for anisole against the total uncorrected peaks for cyclohexyl methyl ether (CHME) for reactions on the metals at different temperatures: ○, palladium at 50° and 75°C; ●, platinum at 0° and 25°C; □, nickel at 50°C.

above the maximum in the anisole peaks. On nickel the maximum of the CHME peaks was 11 to 12 units higher than that of the anisole peaks, in agreement with the expected absence of exchange during deuteration on this metal for the reason that ring exchange was virtually complete before deuteration occurred. The corresponding figures for platinum and palladium were 10 to 13 and 13 to 16, respectively. Thus, exchange during deuteration only took place to a significant extent on palladium. These results resemble those obtained by Harper and Kemball (*20*), who found that more substantial exchange of the ring hydrogen atoms of *p*-xylene occurs during deuteration on palladium than on platinum. The size and pattern of the CHME peaks remained constant for as long as 1 to 2 hr after the anisole had reacted completely on platinum at 25° or palladium at 75°C and so neither further exchange nor hydrogenolysis of the CHME occurs under these conditions.

DISCUSSION

One obvious feature of the results is the low rate of exchange of the hydrogen atoms in the methoxy group of anisole on all three metals. It follows that the ratio of ring exchange to side-group exchange is higher in reactions with deuterium than in those with heavy water (*6, 7*) and although effects of temperature could be important, this suggests that the presence of heavy water may be selectively reducing the rate of ring exchange.

There are very substantial differences between the data obtained on the metal catalysts and the results (*8, 9*) for the homogeneous acid-catalyzed exchange of anisole. Very marked activation at the *ortho* and *para* positions is found in the homogeneous systems, whereas there is comparatively little differentiation between the various ring positions in the heterogeneous exchange reactions. Nickel shows deactivation of the hydrogen atoms in the *ortho* positions but the differences between the reactivity of the five ring atoms are small on platinum and on palladium. The process on the metals is obviously not at all closely related to the type of electrophilic substitution which occurs under acid catalysis in solution.

In many ways the behavior of anisole is similar to the results which are found with alkylbenzenes and deuterium over the metal catalysts. Some data reported by Crawford and Kemball (*3*) for the exchange of ethylbenzene on nickel films at 0°C are compared in Table 8 with our results for anisole. The rates of exchange of the same kinds of ring hydrogen atoms are lower with anisole by factors of not more than 10 but the methoxy group cannot be equated to the β methyl group of ethylbenzene. Multiple exchange is less marked with anisole, although this is to be expected since part of the contribution to M with ethylbenzene is the exchange of the methylene group. Furthermore, the relative rates of ring exchange to deuteration are much the same for anisole on each metal as for the alkylbenzenes. Nickel (*3*) is much more active for exchange than for deuteration but the rates of the two reactions are about the same on platinum and palladium (*20*).

The observation that the order of ring exchange on nickel with respect to the pressure of deuterium is about 1.5 is worthy of comment. The factors which may contribute to a positive order with respect to hydrogen are as follows:

(i) a requirement of a molecule of deuterium or a chemisorbed atom of deuterium to form the activated complex for the rate-determining step; the contributions being first power in the first case and possibly half-power in the second case if the deuterium is weakly absorbed;

(ii) the need to form a relatively weakly adsorbed associative species containing one or perhaps two deuterium atoms more than the type of aromatic species covering most of the surface;

(iii) the need to avoid the formation of a dissociative species containing less hydrogen atoms than the usual adsorbed aromatic molecule and which may compete for sites on the surface to the exclusion of the intermediate involved in the rate-determining step.

TABLE 8
THE EXCHANGE OF ETHYLBENZENE AND OF ANISOLE ON NICKEL FILMS AT 0°C

Ethylbenzene[a]		Anisole	
Hydrogen atoms exchanging	Initial rate[b]	Hydrogen atoms exchanging	Initial rate[b]
meta, para and CH_2 group	422 (M = 3.9)	*meta* and *para*	50, 106 (M = 1.3)
ortho	13	*ortho*	1.6
CH_3 group	1.7	CH_3O group	0

[a] From ref. (*3*).
[b] Rates expressed as D atoms entering 100 molecules min^{-1} 10 mg Ni^{-1}.

We do not have sufficient information available to judge the importance of these various factors in the case of anisole but it seems probable that an associative mechanism of ring exchange is more likely than a dissociative mechanism.

Turning now to the observations on the hydrogenolysis of anisole, we have evidence on platinum that the aryl–oxygen bond reacts more readily than the methyl–oxygen bond and this is in accord with expectation (*10*). Thus, it is not surprising that the hydrogenolysis of anisole occurs at much lower temperatures than the decomposition of diethyl ether in the presence of hydrogen over platinum (*14*) if we ignore the transient initial activity observed with that system. Furthermore, our results show that once the anisole is deuterated to form CHME the carbon–oxygen bonds become less susceptible to hydrogenolysis because no further reaction was observed of this latter compound at 25°C on platinum over 1 to 2 hr. The extent of hydrogenolysis also varies with the metal, being more noticeable on nickel than on platinum and not appreciable on palladium. It is possible that the differences between nickel and platinum are partly connected with the relative rates of deuteration on the two metals; the lower rate of decomposition over platinum may be due to the more rapid conversion of anisole to the less reactive cyclohexyl methyl ether.

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