This quantity is comparable to the data for one-proton exchange determined for other imidazoles. The rate data are summarized in Table IV.

Registry No.—1-Methylimidazole, 616-47-7; 1,3-dimethylimidazolium iodide, 4333-62-4.

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Transfer-Hydrogenation and Transfer-Hydrogenolysis. IV. Catalytic Dehydrogenation by a Quinone

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The dehydrogenation of 2-propanol by chloranil was found to occur in the presence of several transition metal complexes to give acetone and tetrachlorohydroquinone. Some of these reactions seem to be explained by a mechanism that requires both the donor and the acceptor to coordinate simultaneously on the central metal of the catalyst, and hydrogen atoms to be transferred directly from the former to the latter without forming hydride complexes. The dehydrogenation of tetralin and 2,5-dihydrofuran, which are unsaturated compounds, was not influenced by the addition of the metal complexes.

The dehydrogenation of unsaturated compounds by quinones is well known and has been considered to proceed *via* a two-stage ionic process involving a charge transfer complex.[1] The reaction usually requires double bonds or aromatic rings in the hydrogen donors, so that dehydrogenation of saturated heterocompounds by quinones is unusual.[1]

We have found that catalytic hydrogen transfer from 2-propanol[2] or dioxane[3] to olefins proceeds *via* hydride complexes. Moreover, direct hydrogen transfer involving no hydride complex seems not to have been reported in the hydrogenation of olefins[4] or quinones[1,4] catalyzed by transition metal complexes. This study was undertaken to examine the possibility that direct hydrogen transfer can take place from a hydrogen donor to a quinone, without involving a hydride complex, when the reactants do not form a charge transfer complex but are simultaneously coordinated to a transition metal complex.

Results

Hydrogen Donors. As hydrogen acceptor, chloranil was mainly used because of its relatively high thermal stability and hydrogen accepting power. Duroquinone also was used in some cases.

The desirable hydrogen donors for the purpose of this study are those which do not form charge transfer complexes with quinones but do coordinate to transition metals. From this viewpoint, various saturated heteroatom compounds were examined as hydrogen donors.

A hydrogen donor and chloranil (0.25 mol each) and 0.025 mol of $NiBr_2(PBu^n{}_3)_2$ were heated in *o*-dichlorobenzene at 170° for 2 hr. 2-Propanol gave a considerable amount of acetone along with 2-chloropropane. Cyclohexanol and cyclohexyl chloride gave phenol and chlorobenzene, respectively, but the yields were less than 5%. In the reaction of *N*-methylpyrrolidine as a hydrogen donor, neither the expected product, *N*-methylpyrrole, nor unreacted *N*-methylpyrrolidine was detected after the reaction. The same result was obtained in the reaction of the amine at 140°. This observation may be explained by the assumption that the tertiary amine reacted with chloranil.[5] In the reaction of the amine with duroquinone in the presence of $NiBr_2(PBu^n{}_3)_2$, *N*-methylpyrrolidine survived, but *N*-methylpyrrole was not detected.

The reaction in which 2-propanol was used as a hydrogen donor was examined in detail, because the alcohol donated hydrogen catalytically in spite of the formation of 2-chloropropane in a side reaction. For comparison, the reactions of tetralin and 2,5-dihydrofuran, which are unsaturated compounds, were also investigated.

Solvents. To find a suitable solvent, equimolar amounts of 2-propanol and chloranil were heated in several solvents in the presence of $NiBr_2(PBu^n{}_3)_2$ and the reaction mixtures were submitted to gas-liquid chromatographic analysis. The results are summarized in Table I. The solvents of moderate coordinating ability were found to be suitable. Because of the convenience of the analysis, the experiments hereafter were carried out in chlorobenzene.

Dehydrogenation of 2-Propanol. 2-Propanol and chloranil gave acetone, tetrachlorohydroquinone, and 2-chloropropane in the presence of catalysts. The formation of tetrachlorohydroquinone was confirmed by isolation of it as crystals from the reaction mixture and by comparison with an authentic sample. Though the yield of acetone based on the amount of charged chloranil was much higher when 2-propanol was used as hydrogen donor and solvent, the solubility of catalysts in the alcohol was small. The reactions were therefore carried out in chlorobenzene at 170° for 2 hr. The results are summarized in Table II.

Table I
Solvents in the Hydrogen Transfer from 2-Propanal to Chloranil[a]

Solvent	Yield, % Acetone	 2-Chloropropane	Recovered 2-propanol, %
n-Butyl propionate	31	4	29
Bromobenzene	30	7	53
Anisole	26	12	59
Chlorobenzene	25	6	66
p-Chlorotoluene	18	19	53
o-Dichlorobenzene	13	6	57
o-Tolunitrile	12	24	40
Diethylbenzene	8	10	63
Pyridine	1	1	72

[a] 2-Propanol (0.25 mol), chloranil (0.25 mol), and $NiBr_2(PBu^n{}_3)_2$ (0.025 mol) were heated in the designated solvent at 170° for 2 hr.

Table II
Dehydrogenation of 2-Propanol by Chloranil[a]

Catalyst	Registry no.	Yield, % Acetone	 2-Chloropropane	Recovered 2-propanol, %
None		0	0	98
$RhCl(PPh_3)_3$	14694-95-2	76	5	0
$RuCl_2(PPh_3)_3$	15592-49-4	73	5	12
$PdCl_2$	7647-10-1	38	5	56
$PdCl_2(PPh_3)_2$	13965-03-2	31	3	58
$MoCl_5$	10241-05-1	28	27	0
$RuCl_3 \cdot H_2O$	10049-08-8	26	6	8
$NiBr_2(PBu^n{}_3)_2$	15242-92-9	21	6	76
$NiBr_2(PBu^n{}_3)_2$[b]		82	*c*	*c*
$Pt[P(p\text{-tolyl})_3]_4$	34053-78-6	21	4	72
$Al(OPr^i)_3$	51796-09-9	19	4	71
$Pt(PPh_3)_4$	14221-02-4	13	5	72
$PtCl_2(PPh_3)_2$	10199-34-5	12	7	69
$Pt[P(p\text{-ClPh})_3]_4$	51795-66-5	12	1	88
$NiCl_2(PPh_3)_2$		6	9	80
$FeCl_2$(Bipy)		5	1	85
$NiCl_2(PBu^n{}_3)_2$		4	15	71
$PdCl_2(PBu^n{}_3)_2$		4	7	72
$RhCl_3 \cdot 2H_2O$		3	0	96
$CoCl_2(PPh_3)_2$		2	7	77
$RuCl_2(PPh_3)_3 + PPh_3$[d]		0	49	0
$FeCl_2$(*o*-Phen)		0	0	96
Ni(Acac)$_2$		0	0	85

[a] 2-Propanol (0.25 mol), chloranil (0.25 mol), and a catalyst (0.025 mol) were heated at 170° for 2 hr in chlorobenzene. [b] 2-Propanol was used as a donor and solvent. [c] The yield could not measured. [d] Triphenylphosphine (0.25 mol) was added.

The existence of side reactions was shown by the fact that 2-chloropropane was formed and the total amount of acetone, 2-chloropropane, and recovered 2-propanol was less than the amount of charged 2-propanol. When duroquinone was used instead of chloranil under the same reaction conditions in the presence of $NiBr_2(PBu^n{}_3)_2$, $PdCl_2(PPh_3)_2$, $Pt(PPh_3)_4$, or $RhCl \cdot 2H_2O$, neither acetone nor 2-chloropropane was formed, but 2-propanol was recovered quantitatively.

Dehydrogenation of Tetralin. The reactions in which 0.25 mol of tetralin, 0.25 mol of chloranil, and 0.025 mol of a metal complex were heated in chlorobenzene for 2 hr at 160 or 180° were carried out for comparison with the reaction of 2-propanol. In the reaction at 160°, about 0.01 mol of 1,2-dihydronaphthalene and 0.01–0.02 mol of naphthalene were formed; in the one at 180°, 0.01–0.02 mol of 1,2-dihydronaphthalene and 0.05–0.06 mol of naphthalene were detected. No significant effect of the addition of metal complexes was observed in any case, though all of the complexes used in the reaction of 2-propanol were examined. The total amount of 1,2-dihydronaphthalene, naphthalene, and recovered tetralin in the reaction mixtures was almost equal to the amount of charged tetralin in every case. This fact suggests that no side reaction took place in the reaction of tetralin and chloranil. In the reactions in which duroquinone was used instead of chloranil at 180° in the presence of $NiBr_2(PBu^n{}_3)_2$, $Pt(PPh_3)_4$, or $PtCl_2(PPh_3)_2$, 1,2-dihydronaphthalene and naphthalene were not detected and tetralin was recovered quantitatively.

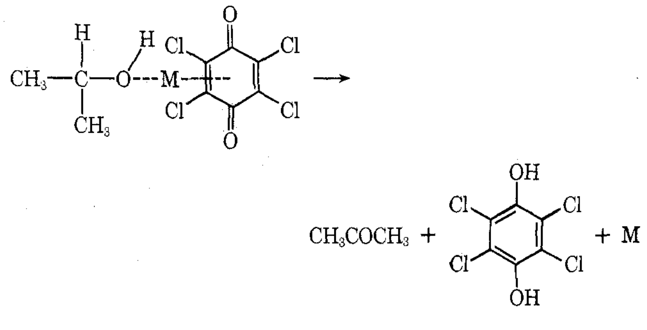
The noncatalytic dehydrogenation of tetralins to naphthalenes by quinones has already been reported.[1]

Dehydrogenation of 2,5-Dihydrofuran. When 2,5-dihydrofuran and chloranil were heated in chlorobenzene at 140° for 2 hr, furan was obtained in 35% yield and the yield was not significantly influenced by the addition of $NiBr_2(PBu^n{}_3)_2$, $NiBr_2(PPh_3)_2$, or $CoBr_2(PPh_3)_2$. It has been reported that 3-phenylfuran was obtained in 10% yield by refluxing 3-phenyl-2,5-dihydrofuran and chloranil in ethylene glycol.[6]

Discussion

The reaction in which 2-propanol was used as a hydrogen donor is obviously catalytic, since the hydrogen transfer reaction did not occur at all in the absence of the metal complexes, and the amount of acetone formed varied greatly for different complexes, as seen in Table II. Two reaction pathways may be considered: (a) hydrogen atoms are transferred in the process of oxidative addition and reductive elimination which involves hydride complexes as is usual for hydrogenation,[4] and (b) the donor and the acceptor are brought together by simultaneous coordination to the central metal of the catalyst, and hydrogen atoms are transferred directly from the donor to the acceptor without involving hydride complexes and without changing the oxidation state of the metal.

In catalytic hydrogen transfer from 2-propanol or dioxane to olefins, the formation of metal-hydride complexes occurs and is the rate-determining step.[2,3] In the transfer-hydrogenation of cyclopentane using 2-propanol as a donor, $RhCl(PPh_3)_3$, $RuCl_2(PPh_3)_3$, and $PtCl_2(PPh_3)_2$ showed catalytic activity under mild conditions, but $PdCl_2(PPh_3)_2$, $NiBr_2(PBu^n{}_3)_2$, $NiCl_2(PPh_3)_2$, and $CoCl_2(PPh_3)_2$ did not catalyze the reaction even after heating in 200° for 4 hr.[2] In the cases of those transition metal complexes that did not catalyze the transfer-hydrogenation of olefins, but did catalyze that of chloroanil, the assumption that hydrogen atoms are transferred directly *via* pathway b seems to be reasonable. Moreover, the assumption may be supported by the fact that the catalytic activity of $Al(OPr^i)_3$ in the reduction of chloranil was comparable to that of some transition metal complexes (Table II), and that Meerwein-Ponndorf-Verley reduction[7] and Oppenauer oxidation,[8] which are catalyzed by the aluminum complex, involve direct hydride transfer from alkoxide ions to coordinated carbonyl compounds.



It is presumed that vacant coordination sites on the metal are needed in this transfer-hydrogenation, since $RuCl_2(PPh_3)_3$ lost its high catalytic activity in the presence of excess triphenylphosphine; the complexes which had bidentate ligands also showed little activity.

When tetralin was used as a donor, the hydrogen transfer reaction was not influenced at all by the addition of metal complexes, suggesting that the reaction proceeds instead *via* change transfer complexes. That 1,2-dihydronaphthalene was always detected in the reaction of tetralin shows that this reaction is stepwise and that the driving force for the dehydrogenation of tetralin is not aromatization.

The dehydrogenation of 2,5-dihydrofuran, which has a heteroatom and a double bond, also was not influenced by the addition of metal complexes, and is again presumed to be a noncatalytic reaction.

Experimental Section

Materials. 2-Propanol, tetralin, 2,5-dihydrofuran, and all solvents were purified by distillation. Chloranil was recrystallized from toluene. Duroquinone, chlorotris(triphenylphosphine)rhodium(I),[10] dichlorotris(triphenylphosphine)ruthenium(II),[11] dichlorobis(triphenylphosphine)palladium(II),[12] dichlorobis(tri-*n*-butylphosphine)palladium(II),[13] tetrakis(triphenylphosphine)platinum(0),[14] tetrakis(tri-*p*-tolylphosphine)platinum(0),[14] tetrakis(tri-*p*-chlorophenylphosphine) platium(0),[14] dichlorobis(triphenylphosphine)platinum (II),[15] dichlorobis(tri-*n*-butylphosphine)nickel(II),[16] dibromobis(tri-*n*-butylphosphine)nickel(II),[16] dichlorobis(triphenylphosphine)nickel(II),[17] dibromobis(triphenylphosphine)nickel(II),[17] dichlorobis(triphenylphosphine)cobalt(II),[18] 2,2′-bipyridinedichloroiron(II),[19] *o*-phenanthrolinedichloroiron(II),[19] and dibromobis(triphenylphosphine)cobalt(II)[18] were prepared by the methods reported in the literature. $PdCl_2$, $MoCl_5$, $RuCl_3 \cdot H_2O$, $RhCl_3 \cdot 2H_2O$, $Al(OPr^i)_3$, $Ni(acac)_2$, 1,2-dihydronaphthalene, 2-chloropropane and tetrachlorohydroquinone were purchased and used without purification.

An Example of Dehydrogenation of 2-Propanol. Chloranil (61.5 mg, 0.25 mmol), 2-propanol (19.1 μl at 25°, 0.25 mmol), and $NiBr_2(PBu^n{}_3)_2$ (15.6 mg, 0.025 mmol) were put into a Pyrex glass tube which had been sealed at one side. Chlorobenzene was added to make the total volume of the solution 1.0 ml. The tube was sealed under vacuum after two freeze-pump-thaw cycles at 10^{-3} Torr on a vacuum line, using liquid nitrogen. The sealed tube was heated for 2 hr in a silicone oil bath kept at 170 ± 1°. Chloranil and the catalyst dissolved slowly at room temperature but quickly at the elevated temperature. Gc analysis was performed at 100° with a Hitachi Perkin-Elmer instrument equipped with a flame ionization detector, using a 2 m × 6 mm stainless column packed with 20% Carbowax on Celite 545. As an internal standard 15 μl of *n*-decane was used. By recrystallization of the resulting precipitate from acetone, pure tetrachlorohydroquinone was obtained, ν_{OH} 3350 cm^{-1} (sharp).

The other dehydrogenation reactions of 2-propanol were carried out in a similar way.

An Example of Dehydrogenation of Tetralin. Tetralin (34.1 μl at 25°, 0.25 mmol), chloranil, and $NiBr_2(PBu^n{}_3)_2$ were treated as in the reaction of 2-propanol described above, except that the reaction temperature was either 160 or 180°. Gc analysis was carried out at 170° using phenylcyclohexane as an internal standard.

An Example of Dehydrogenation of 2,5-Dihydrofuran. Chloranil, 2,5-dihydrofuran (18.4 μl at 25°, 0.25 mmol), and $NiBr_2(PBu^n{}_3)_2$ were treated as in the reaction of 2-propanol, except that the reaction temperature was 140°. Gc analysis was carried out at 100°, using a 2 m × 6 mm stainless steel column packed with 10% silicon DC 11 on Diasolid L. As an internal standard 15 μl of *n*-heptane was used.

Registry No.—2-Propanol, 67-63-0; chloranil, 118-75-2; tetralin, 119-64-2; 2,5-dihydrofuran, 1708-29-8.

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$HCo(CO)_4$ and the Hydroformylation Reaction

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The rate of the stoichiometric hydroformylation reaction and the rate of the decomposition of $HCo(CO)_4$ are affected in a strikingly similar manner by the presence of *p*-methoxybenzonitrile. Apparently this results from a common dependence on the concentration of $HCo(CO)_3$, the key intermediate in both reactions.

The stability and reactivity of $HCo(CO)_4$ are key considerations in both the catalytic and the stoichiometric hydroformylation of olefins. The presence of nucleophiles such as tri-*n*-butylphosphine has a substantial effect on the catalytic process,[1] and in a recent paper[2] we have shown that the presence of *p*-methoxybenzonitrile has a profound effect on the course of the stoichiometric reaction. In the present paper, we show that the presence of *p*-methoxybenzonitrile affects the rate of $HCo(CO)_4$ decomposition in a manner virtually parallel to its effect on the hydroformylation reaction. This parallelism apparently resides in the effect that the nitrile has on the concentration of the key, coordinately unsaturated intermediate, $HCo(CO)_3$, which is in equilibrium with $HCo(CO)_4$.

Experimental Section

A typical reaction was conducted as follows. A toluene solution of $HCo(CO)_4$, prepared and analyzed according to established