Infrared Study of Dehydrochlorination of *tert*-Butyl Chloride on First-Row Transition Metal Chlorides

Earlier, we reported our ESR and ir studies of adsorption of *tert*-butyl chloride (tbc) on CuCl and $CuCl_2$ and concluded that dehydrochlorination of tbc proceeded through an adsorbed *tert*-butyl group and involved surface defects (*1*). We have now extended our ir studies to other first-row transition metal chlorides viz. $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CrCl_3$, and $FeCl_3$. In addition, in the hope of understanding these transition metal chlorides more thoroughly, ir studies of polar nontransition metal chlorides such as $MgCl_2$, $CdCl_2$, and $AlCl_3$ were also carried out.

EXPERIMENTAL

Apart from some minor modifications, the apparatus, sample preparation, and measurement procedure were similar to those described in Ref. (*1*). Unlike the cases of CuCl and $CuCl_2$, the ir spectra of the present nine metal chlorides were accumulated over narrower ranges in order to reduce the time required and the danger of sample deterioration. Moreover, as the background absorptions of these chlorides were found to increase sharply over the range covered, no background subtraction was performed.

For $FeCl_3$ and $CrCl_3$ cases, the pretreatment temperature was 333 and 363 K, respectively, instead of the normal 403 K as the vapor pressures of these two samples were high. Moreover, helium gas was admitted into the sample and reference cells (after gradual reducing tbc pressure to ~0.5 Torr) in order to raise the pressure of the system. This procedure was necessitated for different reasons in the two cases. First, for $CrCl_3$, the rate of the tbc dehydro-

chlorination was found to be much slower than those of other metal chlorides; this is possibly due to slightly different surface structures as suggested by Leung (*2*). During the accumulation process, some surface intermediates might desorb as the catalyst pellet was heated up by the ir beam. In order to reduce desorption of the intermediates (already fewer in number), a higher pressure in the system would be desirable. For $FeCl_3$, however, the tbc dehydrochlorination rate was found so fast that pressure balance in the sample and reference cells was difficult to achieve, hence He gas was deliberately introduced to reduce the tbc dehydrochlorination rate in the sample cell during accumulation process.

RESULTS AND DISCUSSIONS

The spectral regions defined in Ref. (*1*) are adopted here in describing the present results. Also, similar to this previous work, isobutene adsorption studies were carried out as well. However, from preliminary studies of $MgCl_2$ and $MnCl_2$, it was decided that region B (1800–1550 cm^{-1}) offered little information and therefore was not studied for the rest of metal chlorides.

The nine metal chlorides studied can be divided into two groups according to whether or not their ir spectra of surface intermediates exhibit a peak around 890 cm^{-1}. Group I comprises $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $MgCl_2$, $CdCl_2$, and $AlCl_3$. Group II comprises $CrCl_3$ and $FeCl_3$.

Since the appearance of observed ir spectra is rather similar for chlorides of the same group, we shall choose the spectra of $MnCl_2$ and $FeCl_3$ to represent Group I and Group II chlorides, respectively.
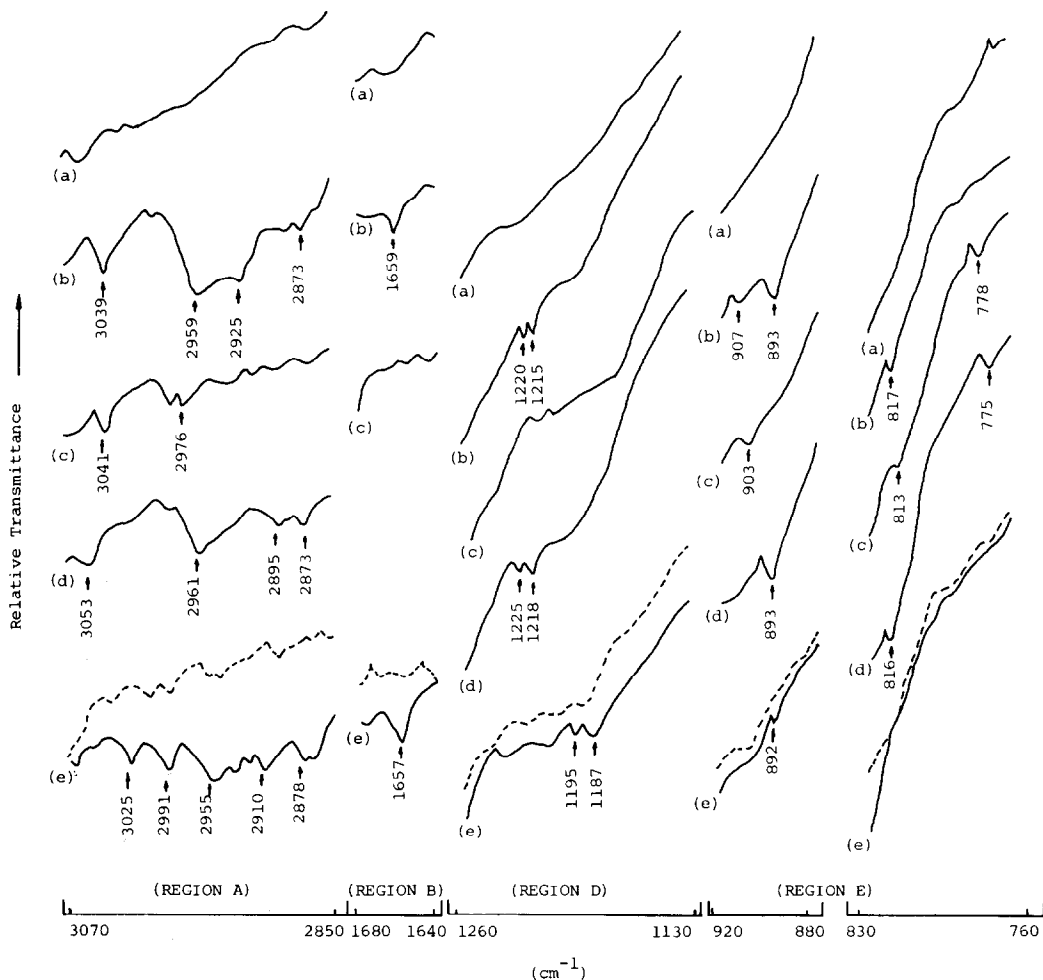
FIG. 1. Infrared spectra of $MnCl_2$ with tbc and isobutene adsorptions (40 times, spectra accumulation in all regions, each ×5). (a) $MnCl_2$ baked at 413 K and pumped to 1×10^{-5} Torr (background). (b) Mn Cl_2 in stage (a) after treatment with 100 Torr tbc at 413 K for 20 min, followed by quenching to R.T. and the pressure of the cells was gradually reduced to ~0.5 Torr. (c) $MnCl_2$ in stage (b) evacuated by rotary pump to 10^{-3} Torr for 2 min. (d) $MnCl_2$ in stage (a) after treatment with 100 Torr tbc at R.T. for 20 min, then the pressure of the cells was gradually reduced to ~0.5 Torr. (e) $MnCl_2$ in stage (a) after treatment with 40 Torr isobutene at 413 K for 20 min, followed by quenching to R.T. and the pressure of the cells was gradually reduced to ~0.5 Torr.

A. Isobutene Adsorption

Infrared study for isobutene adsorption was carried out for all metal chlorides except $FeCl_3$. A typical spectrum is shown in Fig. 1e for the $MnCl_2$ case. The results are summarized in Table 1. On the whole, in region (A), the C–H stretch region, the bands were rather complicated. The bands at 3070, 3053, 3029, 3025, 3020, and 3056

cm^{-1} found in the case of $NiCl_2$, $CdCl_2$, $FeCl_2$, $MnCl_2$, $MgCl_2$, and $CrCl_3$, respectively, appear to correspond to the C—H stretch of the $=CH_2$ group. The absence of peaks around this region for $CoCl_2$ and $AlCl_3$ suggests that isobutene was either only weakly or not adsorbed at all on those two chlorides.

The adsorption of isobutene on the above metal chlorides was supported by the pres-

TABLE 1

Bands Due to Isobutene Adsorption on Various Metal Chlorides

Compound	Region A (3100–2600 cm^{-1})	Region B (1800–1550 cm^{-1})	Region E (1100–700 cm^{-1})
MnCl$_2$	3025(s), 2991(s), 2955(br.s), 2910(br.ms), 2878(br.ms)	1657	892(w)
FeCl$_2$	3029(br.ms), 2972(br.s)	Not studied	893(br.ms)
CoCl$_2$	2965(br.s), 2944(ms)	Not studied	821(v.s.)
NiCl$_2$	3070(ms), 3033(w), 3004(ms), 2951(br.s), 2874(br.ms)	Not studied	—
MgCl$_2$	3020(w), 3006(ms), 2988(ms), 2944(ms), 2890(w), 2833(ms)	1625	886(w)
CdCl$_2$	3053(br.w), 2955(br.s), 2886(w)	Not studied	889(br.ms)
AlCl$_3$	3004(br.ms), 2959(s)	Not studied	—
CrCl$_3$	3056(ms), 2962(ms), 2841(ms), 2817(w)	Not studied	—

ence of a band at 1625 and 1657 cm^{-1} in the spectrum of isobutene adsorption for the MgCl$_2$ and MnCl$_2$ case [the only two cases studied in region (B)], respectively (see Fig. 1e). The small difference between these frequencies and the corresponding frequency of gaseous isobutene suggests that the C=C double bond character of isobutene is retained and the interaction of the adsorbed species with the surface of these chlorides is weak. This deduction is also in accord with the fact that the intensities of the δ_{C-H} mode for MnCl$_2$, FeCl$_2$, MgCl$_2$, and CdCl$_2$ (viz. 892, 893, 856, and 889 cm^{-1}, respectively) were weak when compared to those found in the tbc adsorption. Bands in region (C) (not shown in figure) and (D) are generally rather complex and will not be considered in detail in present work.

B. Intermediate Species of Dehydrochlorination

Infrared spectra for tbc adsorption on all nine chlorides under various conditions are illustrated in Figs. 1 and Fig. 2, and the results are summarized in Table 2.

Two to five bands were observed for all chlorides in region (A) which will be re-

ferred to later. For MnCl$_2$, a band at ∼1659 cm^{-1} was observed in region (B). Comparing the shapes and positions of the adsorbed tbc bands with those of adsorbed isobutene bands, it can be seen that this band might be due to adsorbed isobutene which was released as a product of elimination of tbc on MnCl$_2$ [similar to the 1626-cm^{-1} peak observed in the case of CuCl$_2$ reported in Ref. (1)]. For MgCl$_2$, a band at ∼1626 cm^{-1} was discernible in spite of a broad and intense background band near 1600 cm^{-1} presumably due to traces of strongly retained water; this band (∼1626 cm^{-1}) was probably also due to adsorbed isobutene.

In region (C) (not shown in figures), two to four bands were observed for all the chlorides. The bands around 1480 and 1370 cm^{-1} are probably due to asymmetric scissoring and symmetric scissoring mode of a methyl group, respectively.

In region (D), two to five bands were also observed for all the chlorides. However, the pair of bands at ∼1250 and 1200 cm^{-1}, diagnostic for a *tert*-butyl group was not observed. Thus, unlike the cases of copper chlorides, it appears that the surface inter-
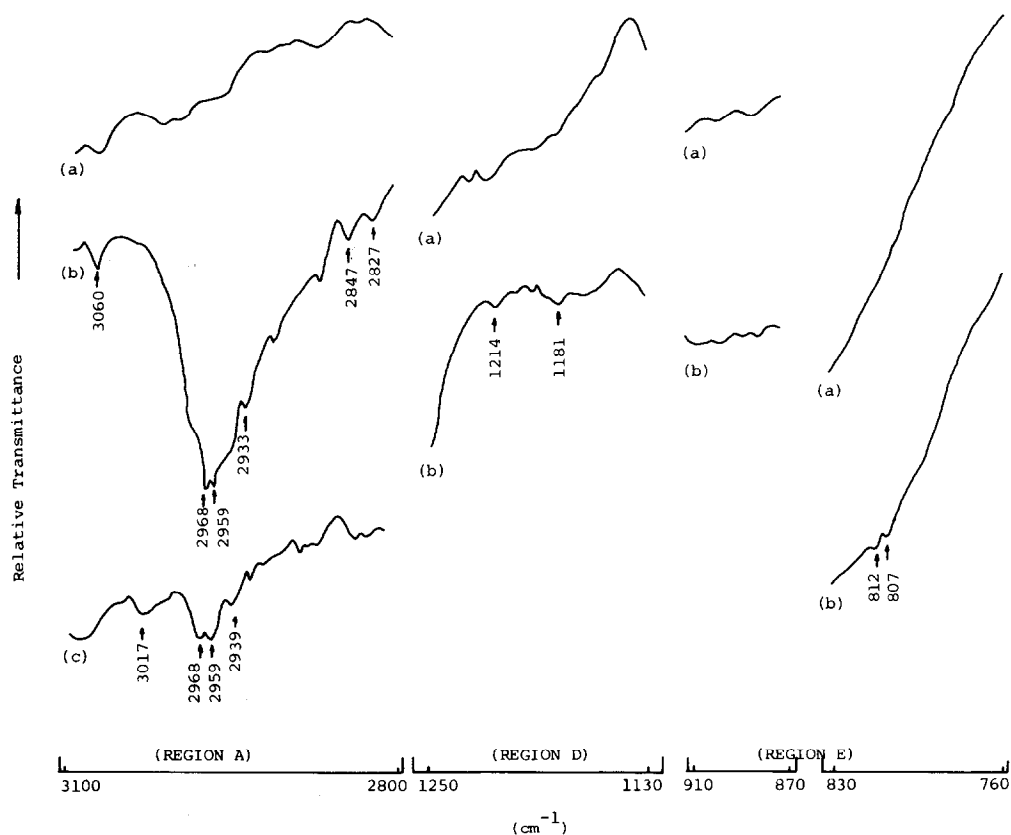
FIG. 2. Infrared spectra of $FeCl_3$ with tbc adsorptions (40 times, spectra accumulation in all regions, each ×5). (a) $FeCl_3$ at 333 K and pumped to 1×10^{-6} Torr (background). (b) $FeCl_3$ in stage (a) after treatment with 108 Torr tbc at 333 K for 15 minutes, followed by quenching to R.T. and the pressure of the cells was reduced to 8×10^{-3} Torr. Helium gas was admitted to the cells gradually to about ~380 Torr. (c) $FeCl_3$ in stage (b) evacuated to 1×10^{-3} Torr for 2 min.

mediate species in the metal chlorides of the present study do not consist of a *tert*-butyl group. The observed bands in this region could well owe their origins to the skeletal mode vibrations of an internal quarternary carbon (*3*).

In region (E), all chlorides except $CrCl_3$ and $FeCl_3$ were found to exhibit band(s) in the range 893–889 cm^{-1}. This is indeed the reason for classifying $CrCl_3$ and $FeCl_3$ differently. The intensities of these bands are much higher than their counterparts in isobutene adsorption. It thus appears unlikely that these bands arose from adsorbed isobutene even though isobutene was the product of the dehydrochlorination of tbc. The origin of bands ~893–889 cm^{-1} could

possibly be due to some reaction intermediates. According to Smith (*4*), the C—H out of plane vibration of a $=CH_2$ group in olefins gives a band at ~890 cm^{-1} with very strong intensity (e.g., in gas isobutene). Thus the relatively intense bands in the region of 893–889 cm^{-1} observed for the Group I metal chlorides might perhaps be due to the δ_{C-H} mode of a

$$\underset{\vdots}{\underset{\text{H}}{\ldots\ldots CH_2}}$$
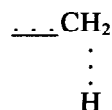
group of an intermediate species. The existence of such a group seems consistent with the presence of high-frequency bands vary-

TABLE 2

Bands Due to tbc Adsorption on Various Metal Chlorides

Cpd	Region A (3100–2600 cm⁻¹)	Region B (1800–1550 cm⁻¹)	Region C		Region D		Region E	
			(1550–1410 cm⁻¹)	(1410–1300 cm⁻¹)	(1300–1150 cm⁻¹)	(1150–1100 cm⁻¹)	(1100–850 cm⁻¹)	(850–700 cm⁻¹)
CuCl	2975(ms), 2962(ms), 2949(vs), 2910(ms), 2870(ms), 2804(w)	—	1492(ms), 1468(ms)	1390(ms), 1383(ms)	1247(ms), 1165(s)	—	—	—
CuCl₂	3060(sh), 3000–2970(brs), 2918(s), 2836(s), 2775(br.sh)	1626(ms)	1445(br)	1379(ms)	1257(w), 1202(sh)	—	Not Studied	Not Studied
MnCl₂	3039(br.s), 2959(br.vs), 2925(ms), 2873(w)	1659(ms)	1513(ms), 1480(br.vs)	1386(s), 1353(br.ms)	1220(ms), 1215(ms)	—	907(w), 893(s)	817(ms), 778(s)
FeCl₂	3029(ms), 2968(br.vs), 2906(ms)	Not Studied	1490(br.ms), 1477(w)	1369(br.s), 1356(sh)	1229(ms), 1199(w)	—	903(w), 893(s)	821(w)
CoCl₂	3018(ms), 2960(br.vs), 2936(s)	Not Studied	1488(ms), 1483(ms)	1367(ms)	1234(ms), 1229(ms), 1212(s), 1206(w)	1127(s)	893(ms)	812(ms)
NiCl₂	3037(br.ms), 2960(ms), 2939(br.s), 2914(ms), 2833(ms)	Not Studied	1497(ms), 1485(ms), 1438(ms), 1419(ms)	1366(s), 1353(s)	1214(ms), 1191(w)	1132(s), 1117(ms)	903(ms), 891(vs)	808(w), 803(br.s), 797(ms)
MgCl₂	3020(br.s), 3004(ms), 2951(br.s), 2910(ms)	1626(s)	1484(s), 1468(s), 1437(w)	1397(ms), 1368(br.vs)	1234(s), 1228(w), 1212(ms), 1196(br.s)	—	893(s), 886(ms)	785(ms), 779(s), 774(ms), 767(w)
CdCl₂	3029(ms), 2945(br.s), 2924(br.s), 2877(ms)	Not Studied	1483(br.s), 1470(w)	1366(ms), 1371(s)	1235(br.ms), 1193(br.vw)	—	892(br.ms)	816(w)
AlCl₃	3058(ms), 2969(vs)	Not Studied	1483(ms), 1466(ms)	1377(br.vs), 1365(br.sh)	1230(s), 1158(br.vs)	—	893(vs)	809(ms)
CrCl₃	3044(ms), 2988(ms), 2971(s)	Not Studied	1482(ms), 1471(ms)	1401(ms), 1381(ms), 1374(ms)	1226(ms), 1201(w), 1182(ms), 1159(vs)	—	—	820(ms)
FeCl₃	3060(ms), 2968(vs), 2959(vs), 2847(ms), 2827(ms)	Not Studied	1510(br.s)	1384(ms), 1376(s)	1214(w), 1181(br.w)	—	—	812(w), 807(w)

ing from ~3058 cm^{-1} (AlCl$_3$) to ~3018 cm^{-1} (CoCl$_2$) in all these chlorides (these frequencies are higher than those expected for ordinary CH$_3$ stretching mode and they are distinguishable from those due to adsorbed isobutene as described earlier).

All nine spectra of the surface intermediates exhibit band(s) in the region (E) around 800 cm^{-1}, varying from ~821 cm^{-1} in the FeCl$_2$ case to ~767 cm^{-1} for MgCl$_2$. These bands might probably be due to C–Cl stretch, as the stretch frequency range of a C–Cl bond is from 850 to 600 cm^{-1}. Another indication of the presence of C–Cl stretch band(s) comes from the absence of *tert*-butyl group in the region (D) established above.

On rough evacuation, the single band at 821 cm^{-1} for FeCl$_2$, and all the three bands (808, 803, 797 cm^{-1}) for NiCl$_2$ disappeared while all the four bands for MgCl$_2$ (785, 779, 774, 767 cm^{-1}) decreased greatly in intensity. This implies that adsorption modes for these three chlorides are rather weak and for the latter two chlorides, the surface bond in the different adsorption modes are probably of similar strength as judged by the small difference in their frequencies.

Of the greatest interest is the MnCl$_2$ case. Samples treated with tbc at 413 K gave only one band at 817 cm^{-1}. After rough evacuation, this band decreased in intensity while a band at 778 cm^{-1} appeared. On the other hand, samples treated with tbc at room temperature gave bands at 817 and 778 cm^{-1}. The large difference in the wavenumber of the two C–Cl stretch frequencies suggests that one intermediate species involves a much weaker C–Cl bond than the other. The variation of intensity of the C–Cl stretch bands under various conditions may be explained by assuming that the intermediate species with a weaker C–Cl bond (stronger surface to chlorine bond) was responsible for the reaction. In the treatment with tbc at 413 K, a greater amount of the intermediate species with the weaker C–Cl bond was used up for dehydrochlorination so that the corresponding

778-cm^{-1} band might become too weak to be observed. As the spectrum accumulation process required quite a long time to complete in our case, some of the intermediate species with strong C–Cl bonds could be transformed into the intermediate species having weak C–Cl bonds. Therefore, the presence of two C–Cl bands in the spectrum after rough evacuation as well as in the spectrum obtained with tbc treatment at room temperature can be explained, since under the conditions when these two spectra were accumulated the dehydrochlorination rate was presumably slow enough to allow significant replenishment of the intermediate species with the weaker C–Cl bond.

On the basis of these ir findings, viz. the absence of a *tert*-butyl group, and the presence of a C–Cl bond and a highly perturbed methyl group, the Structure A
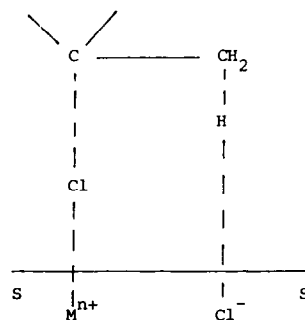
could perhaps be proposed for the surface intermediate. Two points, however, should be noted. First, our data could not confirm the presence of H–Cl$^-$ stretch frequency. Second, for the two Group II chlorides, although no band near 890 cm^{-1} was observed, the structure of the intermediate could still be quite similar to Structure A. In view of the difference in crystal structure and kinetic rate (being very fast for FeCl$_3$ and very slow for CrCl$_3$), it is possible that the methyl group interacts strongly with the surface Cl$^-$ in the former case, and only weakly in the latter, resulting in the absence of the 893-cm^{-1} band.

In conclusion, present ir data enable us

to deduce that tbc is associatively adsorbed onto surfaces during tbc dehydrochlorination on $MnCl_2$, $FeCl_2$, $CoCl_2$, $NiCl_2$, $CrCl_3$, $FeCl_3$, $MgCl_2$, $CdCl_2$, and $AlCl_3$. The resulting surface species—Structure A could possibly be an important reaction intermediate. This is quite different from that reported for CuCl and $CuCl_2$ where tbc is dissociatively adsorbed resulting in a *tert*-butyl group bonded to a surface copper ion. In a forthcoming paper (5), we shall show how the C–Cl stretching frequencies described in this work can be correlated with surface M–Cl bond strength and establish in detail, together with kinetic data, the mechanism of tbc dehydrochlorination on metal chlorides hitherto studied.

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