

Catalytic Activity of Mixed Copper Chlorides (CuCl_x , $1 \leq x \leq 2$)

I. Defect Structure and Catalytic Dehydrochlorination of *tert*-Butyl Chloride

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The catalytic activity of mixed copper chlorides was found to exhibit a double-peak pattern, as before, for the dehydrochlorination of *tert*-butyl chloride. Such a pattern could be correlated with observed structural changes of the two phases. A defect model based on thermal equilibrium of disorder in the two solid phases created by Cu^+ ion diffusion has been proposed. The agreement between the calculated and observed results appears to be satisfactory. If our interpretation were correct, there might well be some other mixed-salts systems (especially halides) which would exhibit nonstoichiometry and "abnormality" in activity pattern or some other physical properties.

INTRODUCTION

In an earlier study on the reactivity and catalytic activity of copper chlorides (CuCl_x , $1 \leq x \leq 2$), Harrison and Ng (*1-3*) found that the catalytic activity of chlorination of propane exhibits a twin-peak behavior w.r.t. x ; and this was tentatively correlated with the amount of a diffusing material, viz., Cu^+ ion in CuCl_2 phase, that was actually a tarnish layer coated on CuCl phase. More work would therefore be called for to further elucidate the nature and function of defects in this catalytic system. In this work, we chose to study the catalytic activity for the dehydrochlorination of *tert*-butyl chloride (tbc)—another reaction that would likely involve the point defect as demonstrated in the works of Simkovich and Wagner (*4*), and Hauffe and Sitabkhan (*5*). Although the CuCl_x samples were also characterized by the X-ray powder technique, the method of preparation differed from the previous work. In the former work, CuCl_x was produced during the chlorination process. Whereas presently, CuCl_x was formed by mixing appropriate amounts of CuCl and CuCl_2 and heated at inert atmosphere to 450°C for a

prolonged period, under these conditions, CuCl melted and flowed over the CuCl_2 particles. Thus, the value of x would be more accurate in the present work. Moreover, since dehydrochlorination does not change the composition of CuCl_x during the course of reaction (at least nominally), activation energy and order of reaction could also be obtained for samples of any value of x .

In part I of this study, defect structure is first identified on the basis of structural change and dehydrochlorination activity. The previous results on propane chlorination will be compared. A mathematical relationship for the defect concentration that would probably be applicable in other mixed-salts systems will be derived in terms of a simple thermodynamic model. The effects of variation of thermodynamic parameters on catalytic activity will be considered. In later parts, other types of data and the kinetic mechanisms of CuCl_x for dehydrochlorination of *tert*-butyl chloride will be discussed.

EXPERIMENTAL METHODS

(A) Reactor for Kinetic Studies

The reactor was a circulating system with a thermal siphon (*6*). The catalyst, in powder form, was placed in glass boats situated

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on glass trays in the central part of the reactor, which was connected through greaseless stopcocks to the high-vacuum system ($\sim 10^{-6}$ Torr) and reactant gas supply, the gas sampler for GC or GCMS analysis, and a spiral gauge. The kinetics were followed by pressure change. GC and GCMS were employed mainly to check the composition of reacting mixtures. All kinetic runs were made after the catalyst samples were heated at the required temperature *in vacuo* for at least 30 min.

(B) Preparation of Catalysts

Pure copper(I) chloride was obtained by treating commercially available copper(I) chloride using the method described by Keller (7). Anhydrous copper(II) chloride was obtained by dehydrating $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ using thionyl chloride (8). The copper chlorides of intermediate compositions were prepared by incorporation of copper (I) and copper(II) chlorides in appropriate proportions at 450°C for 10 h in a sealed glass tube under approximately 1 atm of N_2 . At this temperature, the mixture was a partial melt; presumably copper(II) chloride remained in solid phase whereas copper(I) chloride melted. The so called "pure" CuCl and "pure" CuCl_2 catalyst samples were also heated at 450°C for 10 h under N_2 before use. Physical mixtures M_1 and M_2 were made from CuCl and CuCl_2 samples previously heat treated as indicated above.

(C) Characterization of Catalysts

(i) *Elemental analysis.* The compositions of the copper chlorides before and after reaction (i.e., x in CuCl_x) were determined by total copper and total chloride analysis.

Total copper content was determined by the copper pyridine complex method while total chloride content was determined by the Volhard method.

(ii) *X-Ray powder technique.* A 10.84-cm-diameter Philips camera (Model No. PW1024/00) was used, with Ni-filtered $\text{CuK}\alpha$ radiation, and a 0.5-mm pinhole collimator. All samples were mixed with NaCl

limator. All samples were mixed with NaCl as the internal standard and loaded into a capillary which was subsequently sealed. X-Ray diffraction lines were measured to ± 0.001 cm.

(iii) *Surface area measurements.* A conventional BET apparatus (with N_2 gas) was employed to measure the surface areas of the catalysts, before and after a series of runs.

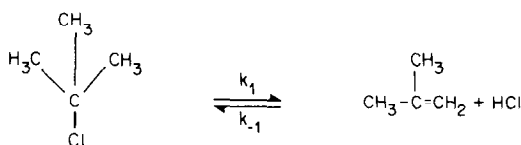
(D) Materials

tert-Butyl chloride was Koch-Light puriss grade (>99%); CuCl was Merck G.R. grade (98% min); $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was BDH Analar (98% min); NaCl was Fluka, A.R.; nitrogen was H.K., oxygen, pure grade.

RESULTS

Catalytic Activity

The dehydrochlorination of tbc on CuCl_x ($1 \leq x \leq 2$)



was studied over a temperature range of 90 – 135°C . Since the reaction is reversible, the initial rate method was used to deduce kinetic parameters. The surface area, the initial rate, the apparent activation energy, and order of reaction obtained for various CuCl_x samples are given in Table 1. It can be seen that for $x > 1.25$, the order is roughly $\frac{1}{2}$, whereas for $x < 1.25$, the order is about 1. The change of order is also accompanied by a change of activation energy which is rather uniform for two regions of x .

The catalytic activity as a function of x in CuCl_x is given in Fig. 1A. The activities for two physical mixtures M_1 and M_2 (i.e., mixed at room temperature) are also shown. The parameter chosen for activity

TABLE 1

x	Specific surface area ($\text{m}^2 \text{ gm}^{-1}$)	Initial rate ^a (Torr sec ⁻¹ /m ²)	E_a (kJ mol ⁻¹)	Order of dehydrochlorination
1.000	3.80	3.17×10^{-4}	48.30 ± 1.80	1.040
1.031	3.83	3.78×10^{-4}	50.16 ± 1.80	1.040
1.110	3.80	4.01×10^{-4}	45.90 ± 1.80	1.060
1.250	3.87	8.80×10^{-4}	47.10 ± 1.80	1.048
1.380	3.82	2.42×10^{-3}	30.76 ± 0.33	0.515
1.451	3.75	3.10×10^{-3}	29.89 ± 0.50	0.512
1.490	3.74	3.89×10^{-3}	31.30 ± 1.80	0.511
1.505	3.96	4.44×10^{-3}	30.93 ± 0.75	0.503
1.536 ^b	3.90	4.08×10^{-3}	—	—
1.562	3.82	3.42×10^{-3}	30.56 ± 0.80	0.501
1.582 ^b	3.80	2.72×10^{-3}	—	—
1.668	3.90	2.86×10^{-3}	29.89 ± 0.50	0.500
1.719 ^b	3.77	3.34×10^{-3}	—	—
1.734	3.73	4.38×10^{-3}	30.39 ± 0.42	0.495
1.755 ^b	3.75	4.38×10^{-3}	—	—
1.796	3.86	3.03×10^{-3}	31.14 ± 0.75	0.490
1.841 ^b	3.83	3.21×10^{-3}	—	—
1.897 ^b	3.86	3.20×10^{-3}	—	—
2.000	3.89	3.33×10^{-3}	31.14 ± 0.50	0.482

^a With initial pressure 36.4 Torr and reaction temperature 110°C.

^b For these samples, only initial rates were measured in order to establish the maxima accurately. So the rates appearing on this table were calculated by assuming a surface area of $3.8 \text{ m}^2 \text{ g}^{-1}$.

is the rate of reaction (per unit area of catalyst) rather than the rate constant because two different apparent orders of reaction were observed for different ranges of x . The double-peak feature of the curve is very distinct, reminiscent of the activity of copper chlorides for propane chlorination (2) which is also included in Fig. 1B.

X-Ray Powder Spectra

X-ray powder spectra obtained show that no structures other than CuCl and CuCl₂ were present in all samples of CuCl _{x} investigated. However, slight shifts in the position of lines were detected for samples with certain x values. The changes were small, but significant enough to suggest that some minor modifications of lattice parameters might have occurred at certain compositions.

Figure 2A shows the lattice parameter a_0 of the cubic CuCl phase in CuCl _{x} as a function of x . Figure 3A shows the lattice

parameters a_0 , b_0 , c_0 of the monoclinic CuCl₂ phase in CuCl _{x} as a function of x . The variation of angle β was found negligible. It should be noted that when $x < 1.4$, the diffraction lines due to CuCl₂ lattice were too weak to render accurate measurements. The same was true for CuCl phase when $x > 1.8$.

Surface Area Measurements

As seen from Table 1, the surface areas of all the catalyst samples were found to fall in a narrow range, viz., $3.8 \text{ m}^2 \text{ g}^{-1}$. No significant change was detected before and after reaction runs for all samples measured. On the other hand, samples of CuCl_{1.000} and CuCl_{2.000} that did not undergo the heat treatment as described under Experimental methods showed different surface areas ($4.99 \text{ m}^2 \text{ g}^{-1}$ for CuCl and $7.15 \text{ m}^2 \text{ g}^{-1}$ for CuCl₂). That is to say, both CuCl and CuCl₂ underwent reduction of surface area after heat treatment at 450°C.

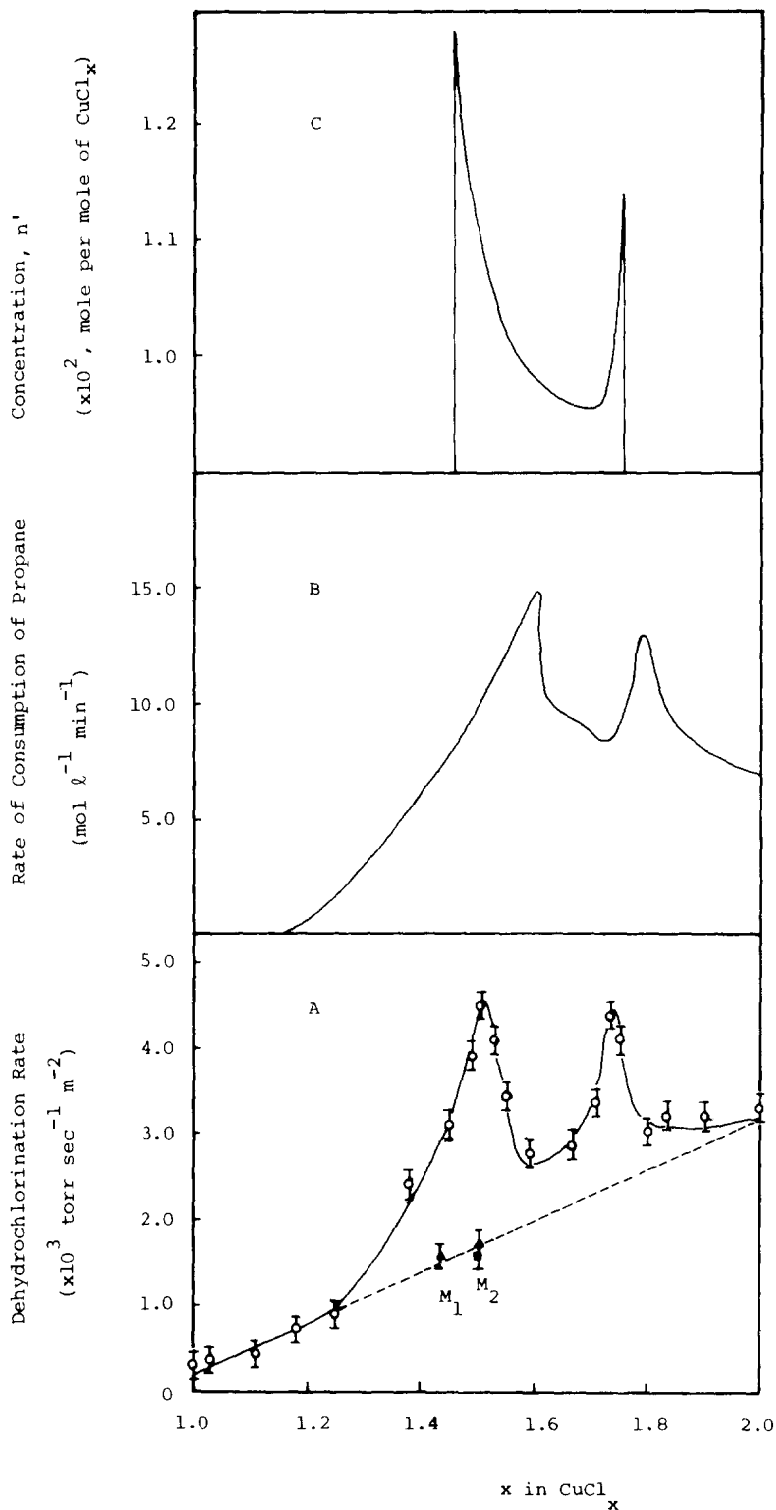


FIG. 1. Catalytic activity and defect concentration of CuCl_x . (A) Dehydrochlorination of *tert*-butyl chloride (initial rate was based on 36.4 Torr initial pressure and at 110°C , Δ are mixtures without pretreatment at 450°C , \square is catalyst prepared at 300°C); (B) chlorination of propane (Ref. (2)); (C) calculated amount of Cu^+ ions migrated from CuCl to CuCl_2 phase.

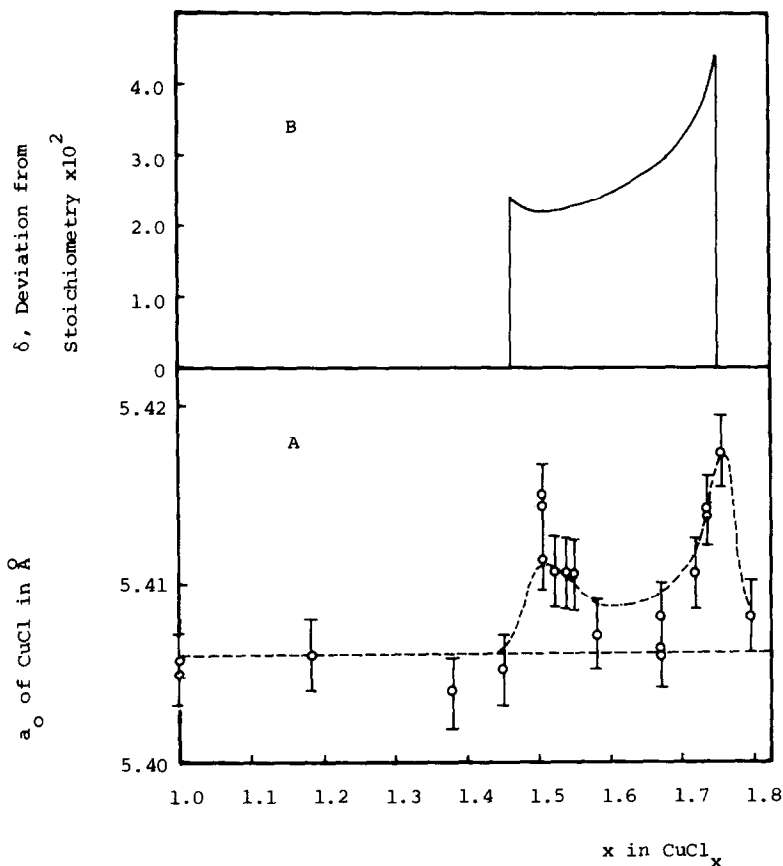


FIG. 2. (A) Lattice parameter a_0 of CuCl in CuCl_x ; (B) calculated amount of deviation from stoichiometry of $\text{Cu}_{1-\delta}\text{Cl}$ in CuCl_x .

DISCUSSION

From the apparent order and the apparent activation energy of the reaction given in Table 1, there are obviously two composition ranges in which different reaction mechanisms are operating. An explanation is that when $x < 1.25$, the reaction occurs primarily on the CuCl phase; this is likely, considering CuCl particles melted over the CuCl_2 particles during the 450°C heat treatment. Beyond $x = 1.25$, the observable kinetics should be dominated by the CuCl_2 phase because of its increasing proportion in the catalyst sample, as well as its relatively higher activity. However, the prominent double peak, a departure of the reaction rate from that expected for a simple

physical mixture of CuCl and CuCl_2 (e.g., M_1, M_2), a priori, can either arise from the CuCl_2 phase itself or be due to the presence of interface between the two halide phases. As pointed out before, Harrison and Ng also observed a double-peak activity pattern for propane chlorination. Their catalyst samples were produced by chlorination of CuCl that was found to obey diffusion kinetics of a tarnish layer which contains a diffusing material, viz., Cu^+ ions, to which the activity was attributed. In the present case, however, the catalyst samples were prepared by partial melting at 450°C in N_2 followed by cooling and grinding. Thus, a tarnish layer should not have developed. Therefore, while it is very interesting to observe the double-peak pattern for an-

other reaction on the CuCl_x catalyst system, the cause for such a behavior remains to be explained.

Thermodynamic Consideration—A Defect Model

Since the CuCl_2 lattice could be thought of as a severely distorted form of the MgCl_2 lattice, an equivalent to that of NaCl in which every (111) plane consists of ions of one sign only (i.e., complete absence of every second plane of cations), when CuCl_2 and CuCl are brought together and if there exists a suitable diffusion path, some copper ions of the CuCl lattice, upon acquiring sufficient thermal energy, may migrate to the CuCl_2 phase, occupying either the second cation plane or some other positions of the lattice. The additional entropy so created will compensate for the enthalpy requirement. If it were assumed that the quantity of each phase remained unchanged and only the interactions between like defects needed to be considered, it could be readily derived (see Appendix) that on mixing the two immiscible solid phases, the equilibrium amount of foreign ion Cu_F^+ (n') in the CuCl_2 phase (which would equal the amount of vacancy \square_{Cu^+} in CuCl phase if there were no extrinsic defects present in either phase) obeys the relationship

$$\frac{n'^2}{(N_\alpha - n')(1 - N_\alpha - n')} = \exp\left[-K + \left(\frac{A}{N_\alpha} + \frac{B}{1 - N_\alpha}\right)n'\right]. \quad (1)$$

Thus n' is a function of N_α , the mole fraction of CuCl_2 phase (i.e., x dependent). All the parameters in the above equation have been defined in the Appendix. Basically, K is the enthalpy increase, whereas A and B are related to the interaction energy of the like defects in CuCl and CuCl_2 phases, respectively. The relative values of these parameters will certainly affect the value of n' for a given N_α . In the Appendix, the solution of Eq. (1) and the effects of varying parameter values are considered in detail. The major points of interest are:

(1) Equation (1) can yield two solutions, one solution, and no solution in different ranges of N_α value. When there are two solutions available, only one has physical meaning. When there is no solution, physically it means that the interaction between defects in the sample of a given N_α becomes so large that stoichiometric CuCl and CuCl_2 phases are regenerated; such a condition is bound to occur when x is either close to 2 or 1.

(2) When $A = B$, i.e., the overall interaction energy due to like defects in both phases is the same, there will be a symmetric n' vs N_α curve with two maxima and a minimum at $N_\alpha = 0.5$ (or for certain K values, three maxima, one of them very shallow, and two minima) (Fig. A2). When $A > B$, there will be a shift of peak positions toward the $N_\alpha = 1$ side; when $A < B$, a shift in the opposite direction will result.

(3) If interactions amongst like defects are ignored, the shape of the n' vs N_α plot is completely different from that described above.

Correlation between Calculated Amount of Cu^+ Ions Migrated and Observed Activity

With the choice of $\Delta H_{\alpha\alpha} = 25.10$ kJ mol⁻¹, $\Delta H_{\beta\beta} = 23.51$ kJ mol⁻¹, $\Delta H = 29.59$ kJ mol⁻¹, and $T = 383$ K (reaction temperature to which activity is referred), the solution of Eq. (1) leads to curve C in Fig. 1.

A comparison between Figs. 1A and C shows that though the position of the first calculated peak is a little on the low- x side, the shape of the saddle in both curves is very similar indeed. Outside the peak-to-peak region, even though the peaks are quite sharp, the observed catalytic activity did not immediately drop to the dotted baseline which would be expected for a shear mixture of "pure" CuCl and "pure" CuCl_2 . This could, however, be accounted for by either the simplicity of our model or the difficulty in achieving perfect thermodynamic equilibrium during the experiment or both.

As the observed values of order and activation energy suggest, the reaction kinetics are dominated by CuCl_2 phase (at $x > 1.25$); it appears that the catalytic activity of CuCl_x could be correlated with the amount of Cu_F^+ that migrated into the CuCl_2 lattice. It should be pointed out that in arriving at this deduction, certain conditions would have to be met. Either the bulk, as well as the surface defects, may be utilized in the reaction mechanism or if surface defects alone can participate, the surface Cu_F^+ concentration follows a pattern of variation similar to that of bulk, or both. The first point could be entertained if the reaction mechanism involved a rapidly transmitted species, viz., either protons or electrons, as first proposed in Ref. (2) and will indeed be taken up further when the reaction mechanism is discussed in Part IV of this work. The second point could only be ascertained one way or another if surface composition data were available. However, while it is true that the surface and the bulk do not necessarily have the same composition, especially during dynamic reaction conditions, the present requirement is actually less severe and there might be a degree of likelihood that it could be satisfied by taking into account the possibility that our experimental conditions could be close to an equilibrium situation.

Naturally, the choice of parameters that yields Fig. 1C is a compromise among various constraints such as the position and relative height of peaks, the deviation from stoichiometry, and the reasonableness of the energy terms.

The process associated with the energy ΔH is actually quite similar to the formation of Frenkel defects. Thus it can be greater or smaller than the energy of formation of Frenkel defects in pure CuCl phase depending on whether it is more or less favorable to place the Cu^+ ions leaving the normal cation site in the interstitials of the same lattice than in some suitable sites in the CuCl_2 lattice. Consequently, the case of creating nonstoichiometry may be smaller

or greater in a mixed-salt condition than in a single salt. Our present calculated values of ΔH and n' probably suggest the latter to be the case. As for the values of interaction energies chosen, they could also be regarded as reasonable (see, e.g., (9)). The fact that mixing the two chlorides at lower temperature did not give rise to nonstoichiometry could mean a high kinetic barrier for diffusion. This point will be considered further later.

It should also be pointed out that in the foregoing treatment we have assumed that the specific surface area of the CuCl_2 phase was more or less unchanged over the whole range of x . This is not necessarily so even though the total surface area of CuCl_x samples measured experimentally shows very little variation for different x values. However, in our opinion, there is no particular reason why this should be the cause for the activity pattern observed.

The next question to deal with is whether or not the extraordinary catalytic activity may arise from some properties of the interface between the two halide phases. It has been shown by Culpin *et al.* (10) that by mixing solid chlorocuprates (I, II), extraordinary optical and electrical behavior could be observed which was accounted for by the intermolecular charge transfer between the CuCl_5^{3-} and $\text{Cu}_5\text{Cl}_{17}^{12-}$ ions. Our present results do not seem to be related to a similar phenomenon because if the abnormally high activity were due to interfacial properties, e.g., some added facility of electron jump between the Cu^+ ions and Cu^{2+} ions at the interface, it is difficult to see any activity pattern other than a curve with a simple maximum at $x \sim 1.5$ (the amount of interface is maximum at this composition as shown in Refs. (10, 11)).

Finally, the earlier work of Harrison and Ng may now be reconsidered in the light of the present results. While the results of propane chlorination could be interpreted in terms of the amount of diffusing material, Cu^+ ions in a layer of CuCl_2 covering a CuCl particle, by comparing Figs. 1B and

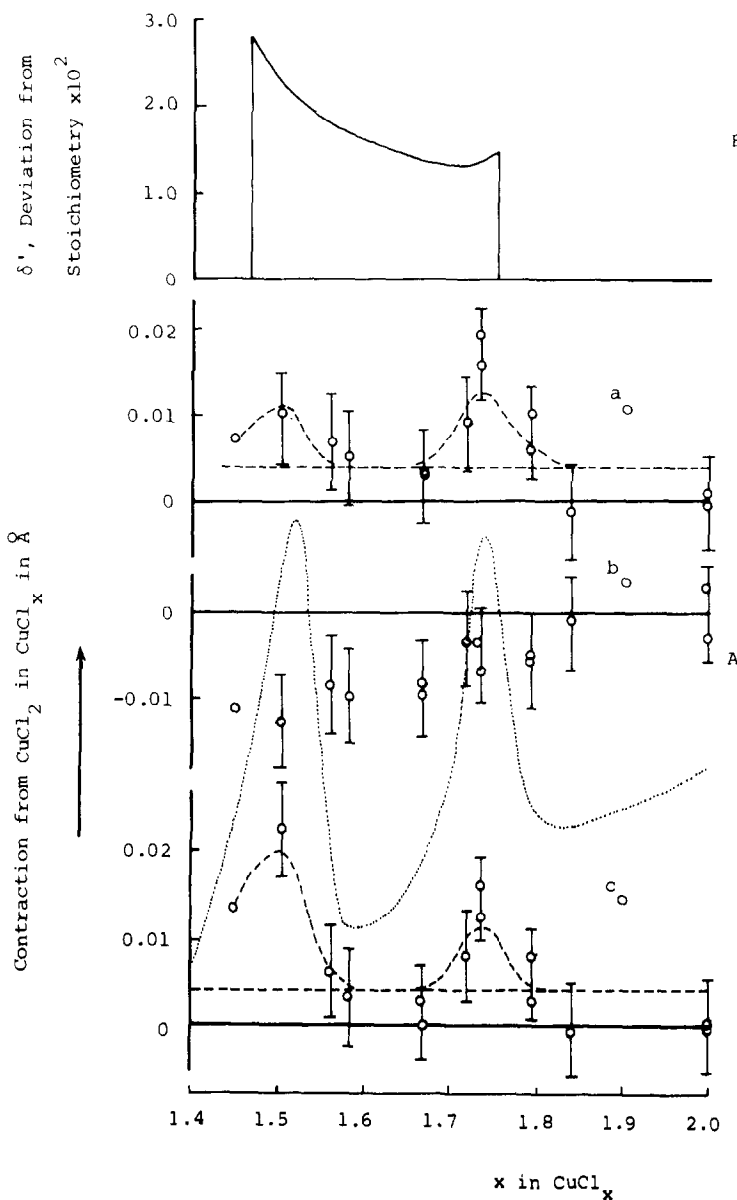


FIG. 3. (A) Lattice parameters of CuCl_2 in CuCl_x ; (B) calculated amount of deviation from stoichiometry of $\text{Cu}_{1+\delta'}\text{Cl}_2$ in CuCl_x .

C, it can be seen that they could be interpreted equally well by the present model. That the two peaks in the activity curve could be less sharp than in the present case should indeed be expected if one takes into consideration the particle size distribution, as well as the conceivably less well-defined thermodynamic conditions. Furthermore, the calculated second peak from the earlier

model (2) is considerably lower and broader than the first peak and there was no parameter one could employ to adjust its shape. In this regard, the two peaks yielded by the present model in fact could fit the kinetic results of propane chlorination even better.

Therefore it seems that both sets of experimental results could be interpreted in

terms of the present model based on the equilibrium amount of Cu^+ ion migrated from one phase to another. The fact that the so-called physical mixture samples exhibit a "normal" activity in both studies illustrates that the kinetic barrier for diffusion is rather high. The tarnish layer in the chlorination study and the partial CuCl coating on CuCl_2 produced by the present method of sample preparation apparently serve a similar function—providing intimate contact for facile diffusion, something probably like grain boundary diffusion. In fact, in the present work, several catalyst samples were mixed at 300°C (a temperature well above the Tammann temperature of CuCl and CuCl_2) and yet they showed almost the same activity as those mixed at room temperature, indicating that the intimate contact resulting from melting is essential for diffusion to take place. Thus, even though the enthalpy increase involved is not high, nonstoichiometry may not necessarily be produced by such a simple mixing process.

Structural Evidence for Present Defect Model

Figure 2A shows that the observed a_0 values of the CuCl lattice remain more or less the same as those for pure CuCl until x reaches approximately 1.47, at which it rises rather sharply to a broad peak. A rather sharp and relatively high peak is also definitely established at $x = 1.76$. In order to correlate with this structural change, it is not the n' value, but rather the degree of disorder that should be considered. From our calculated n' values, the deviation from stoichiometry δ of the $\text{Cu}_{1-\delta}\text{Cl}$ phase can be easily worked out. This is presented as Fig. 2B.

The similarity in the shapes of the two curves in Fig. 2 is impressive, lending support for the validity of the defect model.

The two maxima in the contraction of C_0 at $x \sim 1.5$ and ~ 1.74 are very prominent when compared with the nonstoichiometric extent of the CuCl_2 lattice plotted in Fig. 3B. As for contraction in a_0 , a shallow

bump, admittedly not very definitive, at $x \sim 1.5$ and a rather distinct maximum at 1.75 were observed; but the relative height of the two peaks is not the same as that for δ' . For b_0 , the change is less characteristic, except that there seems to be a general expansion. On the whole, the present set of data compares favorably with those reported earlier (3), except that its features are more distinctive. This is to be expected because the earlier work involved particle size distribution. Indeed, this size distribution effect should prevail over other types of physicochemical studies such as those in Ref. (3).

Since more lattice parameters are involved in CuCl_2 , the effects of stoichiometric deviation on them are not as straightforward as those for CuCl . Nevertheless, as pointed out in Ref. (3), the monoclinic CuCl_2 structure can be regarded as a severely distorted MgCl_2 structure in which a plane containing vacant octahedral sites is present; c_0 transverses this vacant plane, a_0 is related to the distance between adjacent chains, and b_0 is the distance between two adjacent Cu^{2+} ions in a chain. The observed contractions in a_0 and c_0 are therefore consistent with the occupation of the octahedral sites on the vacant plane or the tetrahedral interstitial sites of the CuCl_2 lattice by some cations which either are Cu^+ coming from CuCl lattice or Cu^{2+} displaced from the normal lattice positions. On the other hand, the expansion in b_0 is consistent with the displacement of some Cu^{2+} ions from the normal sites or weakening of bonding in this direction due to additional ions in the lattice. Although our data do not permit the confirmation of either (or both), they are nevertheless not in contradiction with the CuCl results. They clearly could correlate with the dehydrochlorination activity (the background curve).

Finally, it is perhaps noteworthy that the magnitudes of changes in lattice parameters in both CuCl and CuCl_2 phases for the calculated values of δ and δ' compare favorably with those of other nonstoichiomet-

ric compounds, e.g., FeS formed under sulfur pressure (for $\text{FeS}_{1.222}$, $\Delta a_0 = 0.06 \text{ \AA}$) (see Ref. (9)).

Therefore, both CuCl and CuCl_2 results certainly provide evidence for the existence of nonstoichiometric copper chloride phases resulting from Cu^+ ion migration from CuCl to CuCl_2 phase and the validity of the proposed defect model.

CONCLUSION

The catalytic activity of CuCl_x for dehydrochlorination of tbc has been found to be well correlated with structural changes in the CuCl and CuCl_2 phases. These results are compared rather favorably with those calculated on the basis of a model of nonstoichiometry created by a Cu^+ ion diffusion process—the double-peak activity pattern could be attributed to the Cu^+ ions in the CuCl_2 phase. The diffusion barrier for normal copper chloride mixture is apparently very high. It is kinetically possible in the present catalyst samples because of the partial coating of one phase over another that occurred during the preparation process. The calculated results were obtained by a presently derived mathematical relationship that can actually be applied to any binary mixed-salts system. The effects of various parameters on the amount of ionic diffusion (hence deviation from stoichiometry) have been discussed.

The double-peak activity pattern found in the earlier work on chlorination of propane has been reconsidered and also found interpretable in terms of the present defect model. In fact, if our interpretations were correct, it would mean that whenever two immiscible solid phases are brought together and if a constituent of one phase acquires the means to migrate into another, nonstoichiometry might occur and the resulting catalysts might yield a single-peak, double-peak, or even triple-peak (though unlikely) activity pattern for any reaction that might be assisted by defects so created. More work on mixed halides is now in

progress in our laboratory to pursue this point further.

APPENDIX

Formulation of Problem

In a system where two immiscible solid phases are mixed together, it is possible that the amount of each phase remains unchanged while some of the constituent atoms may diffuse from one phase to another. In our present case, we have two solid phases of different structure but the same constituent atoms. As described in the text, copper ions of the CuCl phase would be expected to migrate into CuCl_2 on acquiring sufficient thermal energy. The equilibrium number of foreign copper ions Cu_F^+ in the CuCl_2 phase, n (which equals the number of copper vacancy \square_{Cu^+} in the CuCl phase), could be obtained as follows.

Derivation of Mathematical Relationship

Let α and β represent the CuCl_2 and CuCl phases, respectively; ΔH be the energy required to create a Cu^+ vacancy in CuCl and place the displaced copper ion in the CuCl_2 lattice; $\Delta H_{\alpha\alpha}$ and $\Delta H_{\beta\beta}$ be the energy of interaction between Cu_F^+ ions in CuCl_2 phase and that between \square_{Cu^+} in CuCl phase, respectively, being negative in both cases (attractive); Z , Z' be the number of nearest neighboring Cu_F^+ for each Cu_F^+ and \square_{Cu^+} for each \square_{Cu^+} , respectively; N_α be the mole fraction of α phase; and $(1 - N_\alpha)$ be the mole fraction of β phase.

Then, the enthalpy change of the system following the migration of n copper ions from CuCl to CuCl_2 phase will be given by

$$\Delta H = n\Delta H - \left(n \cdot \frac{Zn}{NN_\alpha} \times \frac{1}{2} \right) \Delta H_{\alpha\alpha} - \left(n \frac{Z'n}{N(1 - N_\alpha)} \times \frac{1}{2} \right) \Delta H_{\beta\beta}, \quad (\text{A1})$$

where N is Avogadro's number.

If it is assumed that the number of sites accommodating n Cu_F^+ ions in the CuCl_2 lattice is the same as that of the normal Cu^{2+} sites, the corresponding entropy

change should be

$$\Delta S = k \ln \left\{ \frac{NN_\alpha!}{(NN_\alpha - n)!n!} \times \frac{(1 - N_\alpha)N!}{[(1 - N_\alpha)N - n]!n!} \right\}. \quad (\text{A2})$$

Thus the free energy change is

$$\begin{aligned} \Delta G = n\Delta H - \left(n \frac{Zn}{NN_\alpha} \times \frac{1}{2} \right) \Delta H_{\alpha\alpha} \\ - \left(n \frac{Z'n}{N(1 - N_\alpha)} \times \frac{1}{2} \right) \Delta H_{\beta\beta} \\ - kT \ln \left\{ \frac{NN_\alpha!}{(NN_\alpha - n)!n!} \times \frac{(1 - N_\alpha)N!}{[(1 - N_\alpha)N - n]!n!} \right\}. \quad (\text{A3}) \end{aligned}$$

To obtain equilibrium value n_e , Eq. (A3) can be differentiated with respect to n and by setting $\delta\Delta G/\delta n$ to zero.

With the help of the Stirling approximation ($\ln n! = n \ln n - n$), one obtains

$$\begin{aligned} \Delta H - \frac{n_e}{N} \left(\frac{Z}{N_\alpha} \Delta H_{\alpha\alpha} + \frac{Z'}{1 - N_\alpha} \Delta H_{\beta\beta} \right) \\ = kT \ln \frac{(1 - N_\alpha - n_e/N)(N_\alpha - n_e/N)}{(n_e/N)^2}. \quad (\text{A4}) \end{aligned}$$

Writing $n' = n_e/N =$ number of moles of Cu^+ ions migrated at equilibrium,

$$K = \Delta H/kT,$$

$$A = Z\Delta H_{\alpha\alpha}/kT,$$

$$B = Z'\Delta H_{\beta\beta}/kT,$$

and

$$\gamma = A/B.$$

Equation (A4) can be rewritten as

$$\begin{aligned} \frac{n'^2}{(N_\alpha - n')(1 - N_\alpha - n')} \\ = \exp \left[-K + \left(\frac{A}{N_\alpha} + \frac{B}{1 - N_\alpha} \right) n' \right]. \quad (\text{A5}) \end{aligned}$$

Equation (A5) can be rearranged to give the following equation, which is conveniently solved by graphical method:

$$2 \ln n' = \ln \beta - K + \alpha n', \quad (\text{A5}')$$

where

$$\alpha = \left(\frac{A}{N_\alpha} + \frac{B}{1 - N_\alpha} \right)$$

and

$$\beta = (N_\alpha - n')(1 - N_\alpha - n').$$

Figure A1 illustrates this method; RHS of Eq. (A5') is a family of curves (different value of N_α). Evidently, the exact relationship between n' and N_α will depend on the relative values of K , A , and B . Thus, mathematically, for a given N_α , there can be two solutions, one solution, or no solution depending on the values of parameters. If n' is to be sensitive to N_α , one must operate in the steep region of $2 \ln n'$ curve. This means k and α must be large or small accordingly.

Solutions of Eq. (A5)—Variation of Parameters

(1) A and B are nonzero and fixed; K varies.

$$(a) \quad A = B \quad (\text{i.e., } \gamma = 1).$$

Setting $A = B = 26.0$, for example, the solution of Eq. (A5) for a number of K values yields the curves in Fig. A2. It can be seen that the solution is not a simple one; three regions of N_α values exist. Using the curve for $K = 9.10$ as an example, two solutions exist for $N_{\alpha_1} < N_\alpha < N_{\alpha_2}$, one for $N_\alpha = N_{\alpha_1}$, $N_\alpha = N_{\alpha_2}$, and none for $N_\alpha < N_{\alpha_1}$, as well as $N_\alpha > N_{\alpha_2}$. It is important to note that the n' values of the upper set (broken line) increases with the increase of K , so they are not real solutions because they are physically disallowed. Outside $[N_{\alpha_1}, N_{\alpha_2}]$, the nonexistence of a solution should mean that the attraction between the like defects becomes so large that the stoichiometric CuCl and CuCl_2 phases are regenerated. Thus experimentally, the lower part of the loop is observable. The two "cutoff" points l, m should correspond to discontinuity values (two maxima or minima) of a physically measurable quantity with which the n' value is correlated. It

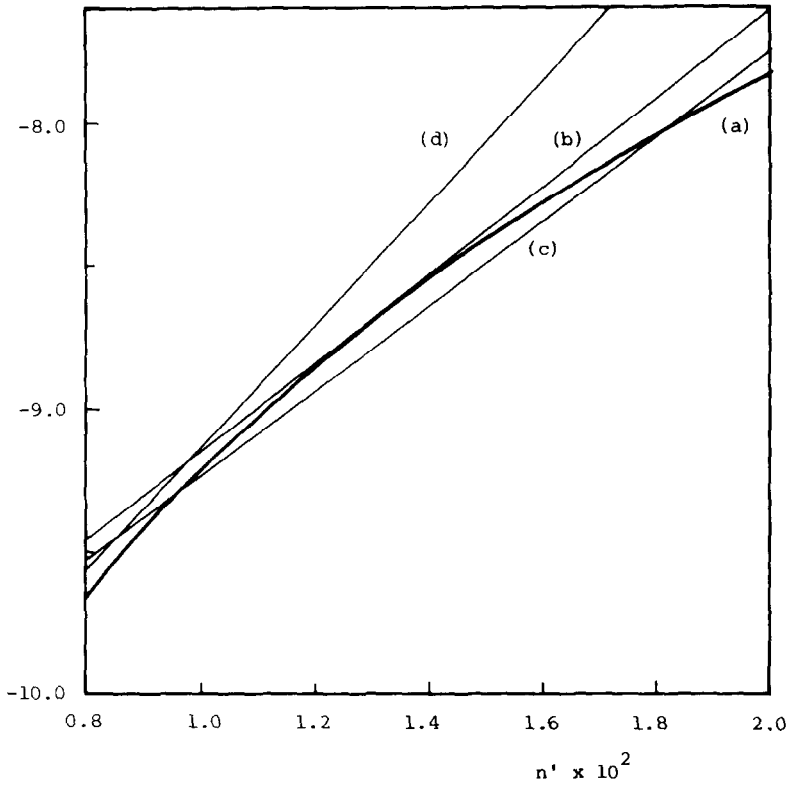


FIGURE A1

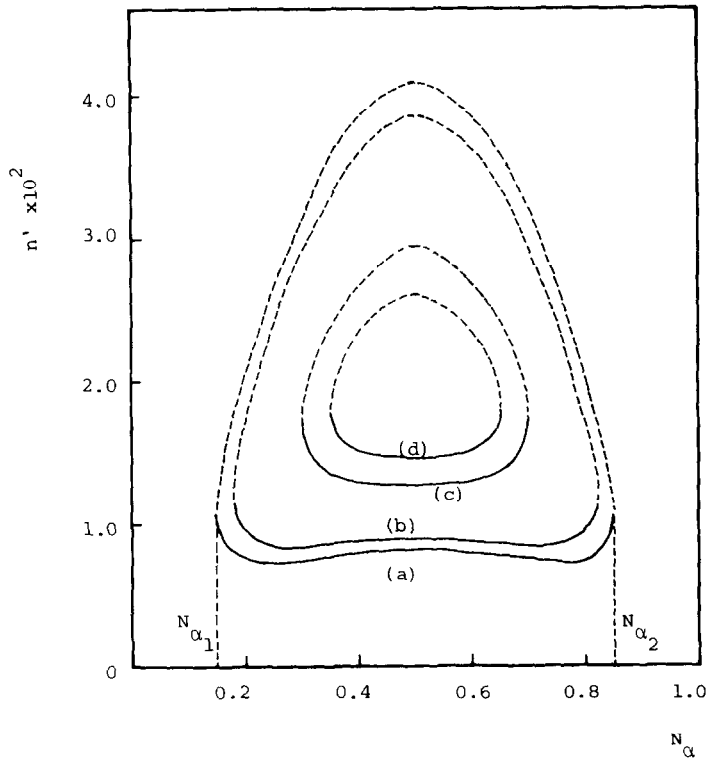


FIGURE A2

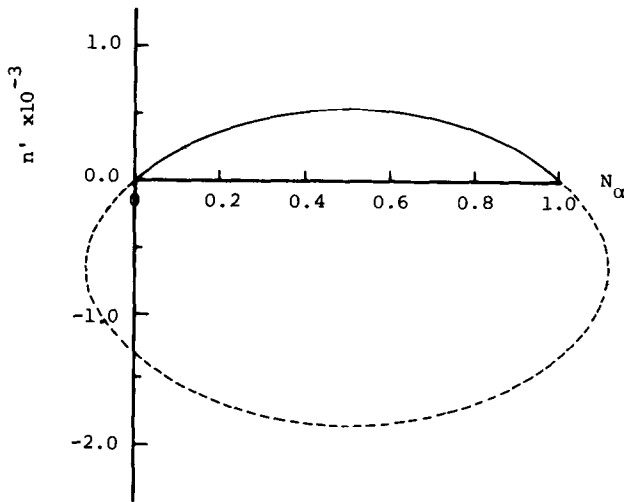


FIGURE A3

should be noted that the very shallow maximum at $N_\alpha = 0.5$ exists only for high K values and they would well be missed in experiments. However, if the measurements are sensitive enough, it is possible to obtain an experimentally measured quantity that exhibits two minima and three maxima w.r.t. N_α .

As for the magnitude of K , the higher its value, the smaller the n' value, but the wider the range of N_α for the solution to exist; consequently the curve will be flatter.

(b) $A \neq B$ (i.e., $\gamma \neq 1$).

When interaction between like defects in α phase is different from that of β phase

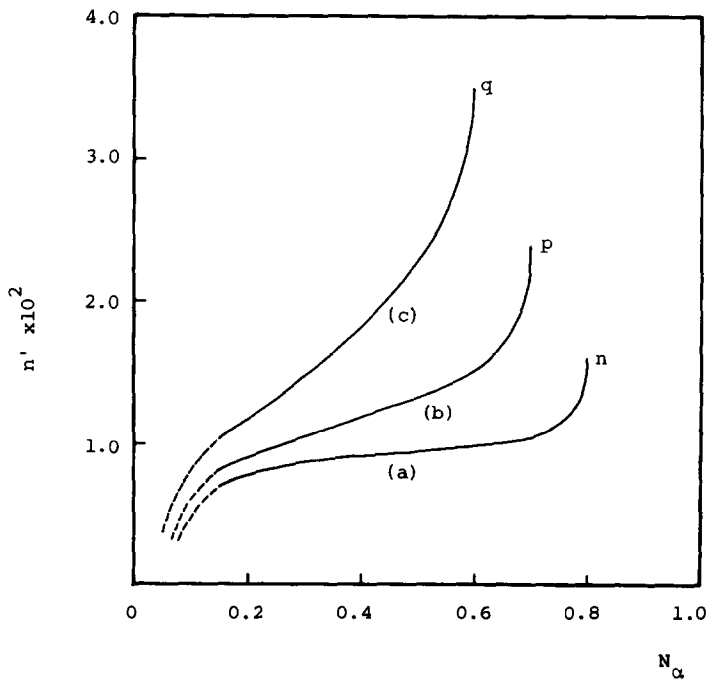


FIGURE A4

(actually a more general case), the n' vs N_α curve is no longer symmetric as in Fig. A2. With $\gamma > 1$, there will be a right shift of the peak positions; with $\gamma < 1$, there will be a left shift. The effect of raising or lowering the magnitude of A or B is the opposite of that of lowering or raising the magnitude of K .

Figure 1C in the text belongs to this case with $A = 6.30$, $B = 5.90$, $\gamma = 1.60$, $K = 9.30$. Of course, only the "real" part of the curve is shown.

(2) $A = B = 0$. This is the case when no interactions between like defects were assumed. Equation (A5) will become

$$\frac{n'^2}{(N_\alpha - n')(1 - N_\alpha - n')} = \exp(-K). \quad (\text{A6})$$

A typical solution of this equation is given in Fig. A3. Naturally, n' values must be positive, so that n' vs N_α plot is a very flat curve with $n' = 0$ at two extremities and a shallow maximum at $N_\alpha = 0.5$.

(3) Either A or B is zero. Equation (A5) will yield a typical solution as shown in Fig. A4. The n' vs N_α plot is monotonic; the points n , p , q represent the cutoff points for different K values. At the other end of M_α , the curves clamp together toward $N_\alpha = 0$.

It is obvious that the foregoing treatment can be extended to other binary mixed-salts

systems. So far, experimental results obtained could only be related to case 1(b). It does not mean of course that it is impossible to find systems for which other cases may apply.

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REFERENCES

1. Harrison, L. G., and Ng, C. F., *Trans. Faraday Soc.* **67**, 1787 (1971).
2. Harrison, L. G., and Ng, C. F., *Trans. Faraday Soc.* **67**, 1801 (1971).
3. Harrison, L. G., and Ng, C. F., *Trans. Faraday Soc.* **67**, 1810 (1971).
4. Simkovich, G., and Wagner, C., *J. Catal.* **1**, 521 (1962).
5. Hauffe, K., and Sitabkhan, F., *J. Catal.* **8**, 340 (1967).
6. Leung, K. S., M. Phil. thesis, University of Hong Kong, 1975.
7. Keller, R. N., "Inorganic Synthesis," Vol. V. McGraw-Hill, New York, 1946.
8. Pray, A. R., "Inorganic Synthesis," Vol. V. McGraw-Hill, New York, 1957.
9. Anderson, J. S., *Proc. Roy. Soc. Ser. A* **185**, 69 (1946).
10. Culpin, D., Day, P., Edwards, P. R., and Williams, R. J. P., *Chem. Commun.*, 450 (1965).
11. Culpin, D., Day, P., Edwards, P. R., and Williams, R. J. P., *J. Chem. Soc. A*, 1838 (1968).