# Adsorption and Conductivity Studies in Oxychlorination Catalysis

Part 3.—The Ethene-Transition-metal Chloride Interaction

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Gas adsorption chromatography (g.a.c.) has been used to obtain isotherms and isosteric heats of adsorption of  $C_2H_4$  at temperatures < 150 °C on VCl<sub>3</sub>, CrCl<sub>3</sub>, CrCl<sub>2</sub>, MnCl<sub>2</sub>, FeCl<sub>2</sub>, CoCl<sub>2</sub>, NiCl<sub>2</sub>, CuCl<sub>2</sub> and CuCl. Physical adsorption is indicated for CrCl<sub>2</sub>, MnCl<sub>2</sub> and CuCl and chemisorption for NiCl<sub>2</sub> and CuCl<sub>2</sub>; the others occupy an intermediate position. The results are discussed in terms of *d*-electron configuration and ion charge/(radius)<sup>2</sup> ratio. G.a.c. studies of C<sub>2</sub>H<sub>4</sub> on PdCl<sub>2</sub>, PtCl<sub>2</sub> and PtCl<sub>4</sub> indicate that chemical reaction occurs at room temperature. For those adsorbents for which heats of adsorption had been obtained, further reaction was initiated by increasing the temperature above 150 °C. Reaction products, *e.g.* HCl, vinyl chloride, dichloroethane and polymers, were identified, where possible, by mass spectrometry or chromatography. The capabilities of a microreactor to study the copper chloride–C<sub>2</sub>H<sub>4</sub> system have been evaluated.

This paper reports the results of  $C_2H_4$  adsorption studies on a wide range of transition-metal chlorides (and MgCl<sub>2</sub>). The investigation was conducted in three main parts. (a) Low temperatures (< 150 °C): gas adsorption chromatography<sup>‡</sup> (g.a.c.) was used to obtain isotherms and isosteric heats of adsorption ( $q_{st}$ ) for those cases where there was no chemical change in the adsorbate. (b) High temperatures (> 150 °C): for those adsorbents for which  $q_{st}$  values had been obtained, the solid was further investigated by increasing the temperature to initiate a reaction and identification of reaction products was by mass spectrometry or chromatography. (c) The capabilities of a microreactor to study the kinetics of the system copper chloride- $C_2H_4$  were evaluated.

# EXPERIMENTAL

#### GAS ADSORPTION CHROMATOGRAPHY

The same apparatus as described in Part 2 of this series was used.<sup>1</sup> All adsorbents were anhydrous and of analytical-reagent grade (Fluka AG:  $CrCl_3$ ; B.D.H.:  $VCl_3$ ,  $CrCl_2$ ,  $CoCl_2$ ,  $NiCl_2$ ,  $PtCl_4$ ,  $PtCl_2$  and  $PdCl_2$ ; ICN Pharmaceuticals:  $MnCl_2$ ,  $MgCl_2$  and 99.999% FeCl\_2;  $CuCl_2$  and CuCl were prepared as in Part 2). During weighing and column packing all materials were handled in a dry box over  $P_2O_5$ . Column resistance was dependent on particle size and for some solids it was found necessary to pre-mix the adsorbent with glass beads (*ca.* 100 mesh, B.D.H.). Ethene (CP Grade, BOC Special Gases) was the only adsorptive used and a sample flask was prepared as in Part 2. Adsorbents were preheated at 250 °C for 1 h.

Elution peaks were analysed as described in Part 2 to obtain isosteric heats of adsorption and isotherms over the temperature range where there was no chemical reaction, typically 50-150 °C.

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‡ Also referred to as gas-solid chromatography.

### 3060

#### **OXYCHLORINATION CATALYSIS**

#### G.A.C. WITH MASS-SPECTROMETRY DETECTION, G.C.M.S.<sup>†</sup>

In g.a.c. the column exit gas passes directly into a flame-ionisation detector or katharometer detector. Replacement of these detectors by a mass spectrometer (Micromass 16F, Vacuum Generators Ltd) allowed the determination of whether there was any chemical change in the injected adsorbate, as well as qualitative identification of reaction products.

#### THE MICROREACTOR

The microreactor was constructed of 4 mm i.d. Pyrex glass and temperature was regulated by an Ether controller/metal-block furnace or a chromatography oven. The adsorptive was pulsed over the catalyst by syringe injection and the pulse was analysed by chromatography. The analysis of the products of the chlorination of ethene was performed by a 9 ft<sup>+</sup> long, 4 mm i.d. glass column of 15% MS 550 silicone oil on Chromosorb W.AW-DMCS 60-80 mesh (Phase Sep Ltd) at 80 °C, with a Pye 104 flame-ionisation or katharometer detector.

For some of the results nitrogen (from a liquid-nitrogen reservoir) was used as the carrier gas with a water trap (type 5A, 30–60 mesh, molecular sieve) and an oxygen trap (manganese oxide, regenerated by heating at 375 °C in hydrogen). Samples were packed and weighed in air, while the ethene sample flask was prepared by thoroughly flushing with nitrogen before injecting a large volume of  $C_2H_4$  into the flask. This was not as satisfactory as flushing with pure  $C_2H_4$  because of the impurities in the nitrogen.

In other cases, helium (grade A, BOC Special Gases) with a drying trap of molecular sieve (type 5A, B.D.H.) was used as the carrier gas. Samples were packed and weighed in a dry box over  $P_2O_5$ , while an adsorptive sample flask was prepared as in Part 2. It was found that the % yield, defined by moles of EDC

% yield = 
$$\frac{\text{moles of EDC}}{\text{moles of } (C_2H_4 + \text{EDC})} \times 100\%$$

where EDC is dichloroethane, varied slightly with the dose size and therefore a constant dose size of  $1 \text{ cm}^3$  was used.

In the calculation of contact time, half of the volume occupied by the catalyst was assumed to be void space. Thus contact time was defined as

contact time =  $\frac{\text{volume occupied by catalyst} \times 0.5}{\text{flowrate}}$ .

# **RESULTS AND DISCUSSION**

#### G.A.C. RESULTS FOR FIRST-ROW TRANSITION-METAL CHLORIDES

In order to evaluate the importance of d electrons to the bonding of ethene, adsorbents of varying d-electron configuration were investigated. However, control experiments were first performed using magnesium chloride as an example of a non-transition-metal chloride and CuF<sub>2</sub>, CuCl<sub>2</sub> and CuBr<sub>2</sub> to investigate the effect of the anion. Elution peaks were narrow and symmetric for MgCl<sub>2</sub>-C<sub>2</sub>H<sub>4</sub> and following the method described in Part 2 a plot of log (net retention time) against reciprocal temperature corresponded to an isosteric heat of adsorption at zero coverage ( $q_0$ ) of 26 kJ mol<sup>-1</sup> (see fig. 1). The only other adsorbent without d electrons to be successfully studied (Part 2) was alumina, Al<sub>2</sub>O<sub>3</sub>, for which  $q_0$  was 26 kJ mol<sup>-1</sup>.

When the cupric salt was changed from the anhydrous chloride to the bromide, after thermal activation at 250 °C for 1 h (a standard procedure for all adsorbents), it was observed by mass spectrometry that some direct bromination and fluorination occurred with ethene at room temperature. Without thermal activation there was no adsorbate-adsorbent interaction. Thus isosteric heats could not be obtained but it can be concluded that changing the anion effects adsorption considerably,<sup>2</sup> in part because

† The assistance of R. Bailey in operating the mass spectrometer is gratefully acknowledged.

 $\ddagger 1 \text{ ft} = 0.3048 \text{ m}.$ 



Fig. 1. Plot of retention time  $(t'_m)$  against  $T^{-1}$  for  $C_2H_4$ -MgCl<sub>2</sub>.

of the differing electronegativity, structural geometry and ion size. Henceforward, only the anhydrous chlorides were studied in order to eliminate this effect and because oxychlorination is really the process of interest.

The results obtained for a series of first-row transition-metal anhydrous chlorides are summarised in table 1. Because of the complicating effect of metal-ion charge, adsorbents were restricted when possible to the +2 valence state. For all the adsorbents, elution peaks were asymmetric, necessitating the construction of isotherms and isosteres as shown for NiCl<sub>2</sub> and MnCl<sub>2</sub> in fig. 2 and 3. The parameter  $n_a$ , the amount of C<sub>2</sub>H<sub>4</sub> adsorbed per gram of adsorbent, is readily converted to surface concentration  $\Gamma$  by dividing by surface area. Assuming an effective cross-sectional area of  $2 \times 10^{-19}$  m<sup>2</sup> for the ethene molecule also allows the fraction of surface coverage  $\theta$  to be estimated; surface coverage fractions were all generally < 0.01.

Specific surface areas by one-point B.E.T. gravimetric analysis (carried out by Winnington Analytical Laboratory, I.C.I.) were generally low, in the range from ca. 2 to 17 m<sup>2</sup> g<sup>-1</sup>.

From table 1 it is evident by comparison with the heat of liquefaction for ethene  $(14.45 \text{ kJ mol}^{-1})$  that for  $\text{CrCl}_2$ ,  $\text{MnCl}_2$  and CuCl there is only physical adsorption of  $\text{C}_2\text{H}_4$ . Chemisorption seems to be occurring for NiCl<sub>2</sub> and CuCl<sub>2</sub>. The adsorption of ethene on VCl<sub>3</sub>, FeCl<sub>2</sub>, CrCl<sub>3</sub> and CoCl<sub>2</sub> is not readily categorised as physical or chemical, being intermediate in magnitude.

adsorbent	isosteric heat of adsorption $q_{\rm st}/{\rm kJ}~{\rm mol}^{-1}$	moles of $C_2H_4$ adsorbed per gram of adsorbent, $n_a/10^{-8}$ mol
VCl <sub>3</sub>	29 27 25	0.5 0.8 1.2
CrCl <sub>3</sub>	42.5 44 26.5 24.5 23.5	1.0 1.5 10 20 30
CrCl <sub>2</sub>	13.5 13	0.2 0.35
MnCl <sub>2</sub>	12 11 11	0.2 0.3 0.4
FeCl <sub>2</sub>	35.5 34 33	0.2 0.3 0.4
CoCl <sub>2</sub>	25 20.5 19	0.15 0.25 0.35
NiCl <sub>2</sub>	52 52.5 53 53.5 54	0.3 0.6 0.9 1.2 1.5
CuCl <sub>2</sub>	58 50 44 44 43	12 29 58.5 88 117
CuCl	13 13 13	1.3 1.95 2.6

Table 1. Isosteric heats of adsorption of  $C_2H_4$  on anhydrous chloride adsorbents

# G.C.M.S. RESULTS FOR PALLADIUM(II) AND PLATINUM(II, IV) CHLORIDES

G.a.c. indicated that for these adsorbents chemical reaction between the surface and the ethene was occurring at room temperature. G.c.m.s. was used to confirm this and identify the products. These solids are of particular interest because of their wide usage as industrial catalysts with alkenes.

For  $PdCl_2$  the mass spectrum for the product (shown in fig. 4) is dominated, excluding the background air spectrum, by a broad peak between mass numbers 21 and 26. This is due to decomposition of a metastable ion, *i.e.* an ion produced in the ion source is unstable and decomposes to a resultant ion of lower mass before detection. However, the original ion may be identified by the position of this broad



Fig. 2. (a) Isotherms for the adsorption of  $C_2H_4$  on NiCl<sub>2</sub> at T = 57.3-102 °C (marked on the curves). (b) Isosteres for the adsorption of  $C_2H_4$  on NiCl<sub>2</sub> at  $n_a = (3-15) \times 10^{-9}$  mol (marked on the curves).



Fig. 3. (a) Isotherms for the adsorption of  $C_2H_4$  on MnCl<sub>2</sub> at T = 43.8-99 °C (marked on the curves). (b) Isosteres for the adsorption of  $C_2H_4$  on MnCl<sub>2</sub> at  $n_a = (2-4) \times 10^{-9}$  mol (marked on the curves).



Fig. 4. Mass spectrum of the products of reaction between  $C_2H_4$  and  $PdCl_2$  at room temperature.

Table 2. Possible combinations causing a metastable peak

original ion	resultant ion	position of metastable peak	
[C₄H₂Cl] <sup>+</sup>	[CC1]+	24.54	
cyclobutane	$[C_3H]^+$	24.45	
cyclobutene	[C <sub>3</sub> ]+	24	
cyclobutene	[C <sub>3</sub> H] <sup>+</sup>	25.35	
[Č₄H,]+	[C,H]+	24.89	
[C,H,Cl,]+	[CH,CI]+	24.75	
[C <sub>2</sub> H <sub>5</sub> ]+	$[C_2H_3]$	25.1	

peak as it is equal to the (mass of resultant ion)<sup>2</sup>/mass of original ion. A  $C_4$  cyclic molecule would be expected to be under strain, with any unsaturated character adding to the tendency of the molecule to undergo decomposition/rearrangment. Inspection of fig. 4 shows the presence of vinyl chloride (VC) and thus the possibility of chlorine cannot be discounted. In table 2 some possible original/resultant combinations are suggested. They all give good agreement with the experimentally observed maximum at 24.7.

Other workers<sup>3-5</sup> have studied the decomposition in solution of  $(PdCl_2C_2H_4)_2$  and reported linear butene formation. Mechanisms involving the coordination structures<sup>6</sup> have been proposed.<sup>3-5, 7, 8</sup>

For PtCl<sub>2</sub> the mass spectrum for the product desorbing from the surface after reaction with  $C_2H_4$  at room temperature did not show any VC but again featured a metastable peak at mass numbers 23–25. Use of lower electric-field potentials again failed to avoid decomposition of the parent ion.

The  $PtCl_2$  used was itself analysed after injections of  $C_2H_4$  by placing it on a silica

#### P. G. HALL, P. HEATON AND D. R. ROSSEINSKY

3065

probe and heating in the ion source at up to ca. 200 °C. The resulting spectrum was that of a polymer hydrocarbon with chain length reaching ca.  $C_{30}$ . The spectrum was free of (i) any chlorine or isotope splitting patterns, (ii) metastable peaks and (iii) any Pt signal. Clearly PtCl<sub>2</sub> would not be of use under these conditions where it has been reported that PtCl<sub>2</sub> does not catalyse the dimerisation of  $C_2H_4^3$  and decomposes on heating above 180 °C to give chlorinated  $C_2$  hydrocarbons.<sup>9</sup> However, other workers have recorded dimerisation and further polymerisation.<sup>4, 5, 8, 10-14</sup>

Platinum(IV) chloride was shown by g.c.m.s. to chlorinate ethene at room temperature. VC, EDC, hydrogen chloride and  $C_nH_xCl$  (where n = 1-4 and x = 0-8) ions were observed. As the reaction temperature was increased  $C_5H_yCl_2$ ,  $C_2H_6$  and  $CH_4$ were additionally formed at 70 °C. At 140 °C further products such as  $C_2Cl_4H_w$  and  $C_7Cl_4H_z$  were seen. It is concluded that the mechanism of interaction between  $C_2H_4$ and PtCl<sub>4</sub> is not like that for PtCl<sub>2</sub>, but is a substitution/radical mechanism.

# RESULTS FOR THE IDENTIFICATION OF REACTION PRODUCTS FROM ETHENE AND FIRST-ROW TRANSITION-METAL CHLORIDES<sup>†</sup>

Two methods of identification were used: (a) the pulse microreactor operated with a chromatographic separating column and (b) g.c.m.s. The first method was least satisfactory because hydrogen chloride created spurious peaks by reaction with the separating column and caused tailing by attacking the katharometer detector. However, g.c.m.s. has the disadvantage that only reaction temperatures < 200 °C could be studied.

The results obtained by methods (a) and (b) are given in tables 3 and 4, respectively. The two techniques show that: (i) VCl<sub>3</sub> is very volatile at high temperature, which makes product identification difficult, and at 250 °C some vinyl chloride (VC) was observed but it is not known if 1,2-dichloroethane (EDC) was formed, (ii) CrCl<sub>3</sub> forms VC and EDC at 250 °C, but a hydrocarbon polymer (non-chlorine-containing) was also formed, (iii) there is no reaction between NiCl<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> at < 350 °C and (iv) CuCl<sub>2</sub> predominantly forms EDC above 150 °C with little VC until above 300 °C, although a mass spectrum which has been completely analysed<sup>15</sup> showed the chlorine isotope splitting patterns, clearly identifying the products.

# MICROREACTOR RESULTS FOR COPPER(I, II) CHLORIDE-ETHENE

The effectiveness of the microreactor was found to be dependent on the precision of the temperature thermostatting and the absence of oxygen. When the catalyst temperature was regulated by an Ether controller and block heater, the temperature oscillated by  $\pm 3$  °C with gradients inside the sample. Direct chlorination of C<sub>2</sub>H<sub>4</sub> by CuCl<sub>2</sub> was very temperature sensitive between 230 and 270 °C, the yield trebling every 20 °C. Thus for isothermal experiments scatter in the results was observed.

At 250 °C, EDC was the only major product from injections of ethene over *ca*. 0.5 g of copper(1, 11) chloride. The yield was dependent on  $[Cu^{2+}]$  and never greater than 2% for a contact time of *ca*. 0.2 s. The small yield represents an advantage of the pulse mode of operation since experiments can be carried out at an effectively constant solid composition.

The yield of EDC from copper(1) chloride (containing small amounts of  $Cu^{2+}$ ) was very sensitive to oxygen. There were experimental problems in excluding oxygen totally, particularly from the sample flask and the results seemed dependent on the success in excluding it.

The effect of pretreating copper(II) chloride with  $HCl+O_2$  and  $O_2$  at 250 °C to remove any  $Cu^+$  was investigated. The initial yield of EDC after pretreatment

† The assistance of N. Warrender is gratefully acknowledged.

solid	reaction temp./°C	reaction products		
		VC	EDC	other
VCl <sub>3</sub>	250			
	300	$\checkmark$	unknown	$\checkmark$
CrCl <sub>3</sub>	250	$\checkmark$	$\checkmark$	$\checkmark$
0	300	$\checkmark$	unknown	1
	350	$\checkmark$	unknown	$\checkmark$
NiCl,	250	_		
2	300			
	350			_
CuCl,	50			
2	100	_	_	
	150	_		
	200		$\checkmark$	
	250		$\checkmark$	
	300	_	$\checkmark$	
	350	$\checkmark$	$\checkmark$	-
	400	$\checkmark$	$\checkmark$	$\checkmark$

# Table 3. Identification of reaction products from anhydrous metal chlorides and ethene by use of a microreactor with chromatographic detection

# Table 4. Identification of reaction products from anhydrous metal chlorides and ethene by use of g.c.m.s.

	reaction temp./°C	reaction products				
solid		HCl	VC	EDC	other	
VCl <sub>3</sub>	40	$\checkmark$	no	no	solid decomposition	
CrCl <sub>3</sub>	35 100	~			polymer	
NiCl <sub>2</sub>	50 125 200					
CuCl <sub>2</sub>	50 110 150 210					

generally was found to be smaller and increased with increasing number of ethene injections, whereas the overall tendency was for the yield to decrease slightly as  $[Cu^{2+}]$  fell, provided no regenerative pathways were available.

The selectivity of the chlorination reaction in producing EDC was always high (>95%) but occasionally other products were observed: (i) vinyl chloride, presumably from the thermal cracking of EDC [this also suggests that hydrogen chloride must be present (not detected by f.i.d.)] and (ii) methylene chloride, possibly from

#### P. G. HALL, P. HEATON AND D. R. ROSSEINSKY



$$2CuO \cdot CuCl_2 + C_2H_4 \rightarrow 2Cu_2 + 2CH_2Cl_2$$

as this is consistent with a pink/red coloration of the solid afterwards.

When the thermostatting of the microreactor was controlled by an oven, isothermal experiments were possible to an accuracy of  $\pm 0.5$  °C. Results obtained were reproducible to within 8% and devoid of significant scatter.

The first property of the  $\text{CuCl}_2-\text{C}_2\text{H}_4$  system to be examined was the change in yield of EDC with contact time. Variation of the flowrate over the catalyst effectively changes the extent of reaction and therefore reaction order can be determined. The first-order plot of  $\ln [a/(a-x)]$  against t at 250 °C (shown in fig. 5), where a is the number of moles of reactant that undergo reaction in time t, showed that the rate constant was  $4 \times 10^{-2} \text{ s}^{-1}$ , indicating that the chlorination of  $\text{C}_2\text{H}_4$  to EDC at 250 °C is a fast process.

Freshly prepared copper(I) chloride gave no detectable yield of any product with  $C_2H_4$  at 250 °C.

The change in catalyst activity with age is shown in fig. 6. It appears that the activity stabilises after 6 h. A sample of  $CuCl_2$  heated at 250 °C for 40 h showed a decrease in surface area<sup>†</sup> from 3.2 to 2.9 m<sup>2</sup> g<sup>-1</sup>. The effect of sintering would therefore appear not to be important. However, heating will also cause some disproportionation of  $Cu^{2+}$ .

Further kinetic work has been carried out<sup>‡</sup> with at least 6 h being left for activity to stabilise before injections of  $C_2H_4$  were made. The variation of yield with temperature was established<sup>15</sup> and yield against contact time data were collected at several temperatures. The activation energy for the chlorination of  $C_2H_4$  to EDC was determined to be  $40 \pm 4$  kJ mol<sup>-1</sup>.

- † Determined by gravimetric N2 adsorption by Winnington Analytical Laboratory, I.C.I.
- ‡ The assistance of N. Warrender is gratefully acknowledged.



Fig. 6. Change in catalyst  $(CuCl_2)$  activity with age at 250 °C.

# DISCUSSION

A range of reaction products has been identified (1,2-dichloroethane, vinyl chloride, dimers and hydrocarbon polymers), but no catalyst has been seen to rival  $CuCl_2$  in the selective formation of 1,2-dichloroethane.

The microreactor has demonstrated its potential for qualitative and quantitative work. However, results seem to depend on experimental conditions, *e.g.* method of thermostatic control, degree of oxygen exclusion, sample pre-treatment and dose size.

# THE *d*-ELECTRON CONFIGURATION FOR FIRST-ROW TRANSITION-METAL CHLORIDES

The results described above compare the strength of the  $M-C_2H_4$  bond, as reflected by the isosteric heat of adsorption  $q_{st}$ , for a range of transition metals M. Weak bond strengths are not readily measured and therefore the heat of adsorption is a valuable guide. To simplify the data of table 1,  $q_{st}$  values were extrapolated to the zero coverage value  $q_0$ , with the uncertainty in  $q_0$  being a function of the variation of the measured  $(q_{st}, n_a)$  values in table 1. Fig. 7 shows the variation of  $q_0$  with the number of *d* electrons and indicates that the bonding of  $C_2H_4$  is not favoured by  $d^4$ ,  $d^5$  and  $d^{10}$  configurations. This may be explained by the molecular-orbital bonding approach as follows: (i) a  $d^5$  high-spin octahedral metal ion will have no completely filled orbitals to participate in back-bonding into the empty  $\pi^*$ -antibonding orbitals of ethene, nor any completely empty orbitals to accept the  $\pi$  electrons of ethene, (ii) a  $d^4$  Jahn– Teller-distorted high-spin ion will have no completely filled orbitals for back-bonding, nor appreciable  $\sigma$ -bonding as the  $d_{z^2}$  orbital is partially filled, and (iii) a  $d^{10}$  molecule will have complete back-bonding but the fully occupied orbitals will not favour  $\sigma$ -bonding to  $C_2H_4$  by acceptance of  $\pi$  electrons.

However, this argument does not explain the large change in  $q_0$  between  $d^9$  and  $d^{10}$ .



Fig. 7. Isosteric heats of adsorption of  $C_2H_4$  on transition-metal chlorides: effect of *d*-electron configuration. ( $\Delta_{k}^{l}H$  is the heat of liquefaction of  $C_2H_4$ .)



Fig. 8. Isosteric heats of adsorption of  $C_2H_4$  on transition metal chlorides: effect of charge/(radius)<sup>2</sup>.

In fact  $d^{10}$ -ethene complexes are often stable because of the electronic configuration, e.g.  $[Ag(C_2H_4)]^+$  with  $\sigma$ -bonding to the unoccupied 5s orbital; the bonding molecular orbitals allow a variety of ethene-transition-metal-ion orientations.<sup>16</sup>

# THE ION-POLARISING EFFECT

The g.a.c. results in Part 2 established that the unsaturated nature and therefore the higher polarisability of the adsorbate was important. For a constant adsorbate, *i.e.* ethene, it is possible to understand the results of fig. 7 further using the ion-polarising effect in terms of the ratio of the ionic charge/(ion radius)<sup>2</sup>.

Assuming for representation purposes only a physical interaction, fig. 8 shows  $q_0$  plotted against  $e/r^2$  for the first-row transition-metal chlorides (and MgCl<sub>2</sub>): it is seen that the majority of them lie fairly close to a common line through the origin, presumably corresponding to the polarisation effect on C<sub>2</sub>H<sub>4</sub>. Cu<sup>+</sup> lies above the line because the van der Waals forces probably do not permit  $q_0$  to fall much below the heat of liquefaction (14.45 kJ mol<sup>-1</sup>). Mn<sup>2+</sup> lies below the line for reasons explained earlier. Since the value of  $q_0$  for CoCl<sub>2</sub> was  $30 \pm 5$  kJ mol<sup>-1</sup>, Co<sup>2+</sup> may well lie close to the line. Good agreement is seen for Mg<sup>2+</sup>, Cr<sup>2+</sup>, V<sup>3+</sup> and Cr<sup>3+</sup>, thus only for FeCl<sub>2</sub>, NiCl<sub>2</sub> and CuCl<sub>2</sub> are other factors altering  $q_0$ , such as electronic configurations allowing for back-bonding.

 $PdCl_2$ ,  $PtCl_2$  and  $PtCl_4$  gave  $q_0$  values > 65 kJ mol<sup>-1</sup> and therefore have a greater interaction with  $C_2H_4$  than can be accounted for by the polarisation effect. These salts are known to have different crystal structures than those of the other chlorides, which suggests that structure may be a major factor.

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- <sup>1</sup> P. G. Hall, P. Heaton and D. R. Rosseinsky, J. Chem. Soc., Faraday Trans. 1, 1984, 80, 2785.
- <sup>2</sup> E. R. Gilliland, J. E. Seebold, J. R. Fitzhugh and P. S. Morgan, J. Am. Chem. Soc., 1960, 61, 1939; J. S. Anderson, J. Chem. Soc., 1934, 971.
- <sup>3</sup> J. T. van Gemert and P. R. Wilkinson, J. Phys. Chem., 1964, 68, 645.
- <sup>4</sup> A. D. Ketley, L. P. Fisher, A. J. Berlin, C. R. Morgan, E. H. Gorman and T. R. Steadman, *Inorg. Chem.*, 1967, 6, 657.
- <sup>5</sup> R. G. Schultz and D. E. Gross, Adv. Chem. Ser., 1968, 70, 97.
- <sup>6</sup> J. N. Dempsey and N. C. Baenziger, J. Am. Chem. Soc., 1955, 77, 4984.
- <sup>7</sup> C. M. Harris and S. E. Livingstone, Rev. Pure Appl. Chem., 1962, 12, 16.
- <sup>8</sup> Y. Kusunoki, R. Katsuno, N. Hasegawa, S. Kurematsu, Y. Nagao, K. Ishii and S. Tsutsumi, *Bull. Chem. Soc. Jpn*, 1966, **39**, 2021.
- <sup>9</sup> A. S. Gow and H. Heinemann, J. Phys. Chem., 1960, 64, 1574.
- <sup>10</sup> J. Smidt, W. Hafner and J. Sedlmeier, British Patent 887362, 1963; Chem. Abs., 1963, 58, 3521e.
- <sup>11</sup> R. S. Berger and E. A. Youngman, J. Polym Sci., Part A, 1964, 2, 357.
- <sup>12</sup> N. Phung and G. Lefebvre, C.R. Acad. Sci., Ser. C, 1967, 265, 519.
- <sup>13</sup> F. N. Jones, J. Org. Chem., 1967, 32, 1667.
- <sup>14</sup> H. C. Volger and K. Vrieze, J. Organomet. Chem., 1968, 13, 495.
- <sup>15</sup> N. Warrender, internal report, Exeter University, 1981.
- <sup>16</sup> J. W. Moore, Acta Chem. Scand., 1966, 20, 1154.

#### (PAPER 4/269)