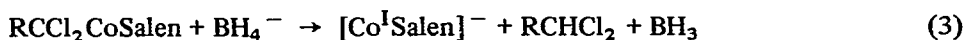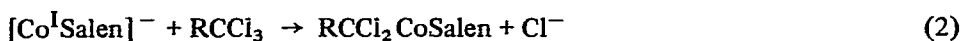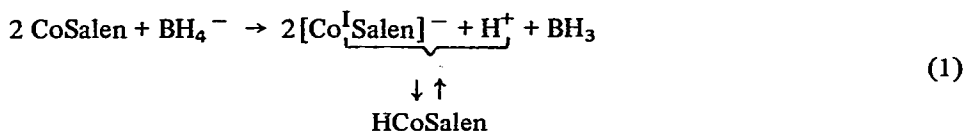## Preliminary communication

Organometallic intermediates in the homogeneous catalytic reduction of *gem*-trichloroalkanes in the presence of a Schiff's base cobalt complex

I.Ya. LEVITIN, M. DVOLAITZKY and M.E. VOL'PIN

Institute of Organo-Element Compounds, Academy of Sciences, Moscow (U.S.S.R.)
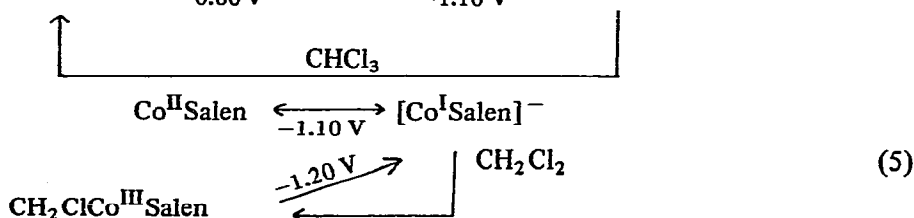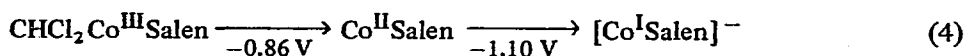
(Received June 23rd, 1971)

We have found that bis(salicylidenato)ethylenediaminecobalt (CoSalen) is an effective catalyst for the reduction of chloroform and 1,1,1-trichloroethane with sodium borohydride in DMF at room temperature to give the respective dichlorides in good yields, $CHCl_3$ being converted to CH_2Cl_2 (68%) and CH_3CCl_3 to CH_3CHCl_2 (84%). Under the same conditions *gem*-dichlorides, as well as monochloroalkanes, appeared unreactive. Such an observation does not, however, fit into the general pattern of transition metal catalysis for in the reduction of organic substrates with hydrides the catalyst is usually assumed[1,2] to provide a fast electron transfer from the two-electron donor to the one-electron acceptor. Reduction of CoSalen with sodium borohydride occurs very slowly, and for this reason $NaBH_4$ + CoSalen failed to reduce a typical one-electron oxidant such as nitrobenzene. It appears therefore that the original divalent complex should be a precursor of a catalytically active species rather than take part in the catalytic cycle. This condition is satisfied in the following reaction scheme:

$$2 \text{ CoSalen} + BH_4^- \rightarrow 2[\text{Co}^I\text{Salen}]^- + H^+ + BH_3$$

$$\downarrow \uparrow$$

$$\text{HCoSalen}$$

(1)

$$[\text{Co}^I\text{Salen}]^- + RCCl_3 \rightarrow RCCl_2\text{CoSalen} + Cl^- \qquad (2)$$

$$RCCl_2\text{CoSalen} + BH_4^- \rightarrow [\text{Co}^I\text{Salen}]^- + RCHCl_2 + BH_3 \qquad (3)$$

Here the catalysis is preceded by the slow reduction of the initial complex (eqn. 1), both the reduced complex $[\text{Co}^I\text{Salen}]^-$ and the organometallic compound $RCCl_2\text{CoSalen}$ being involved in the catalytic chain (eqns. 2, 3). Evidence for this mechanism has been provided by a kinetic study of the reduction of chloroform and 1,1,1-trichloroethane, together with an investigation of the polarographic behaviour of cobalt complexes involved in a catalytic system. The rate of reduction of trichloroalkanes increases as the storage time of the CoSalen/borohydride solution increases before the addition of substrate in accordance with eqns. 1–3. The gradual increase in the number of catalytically active

particles in the system also accounts for the autocatalytic shape of the kinetic curves obtained (Fig.1). The rate of reduction of 1,1,1-trichloroethane is decreased if a small amount of isoamyl chloride is introduced into the system before addition of the substrate. Since the added alkyl halide reacts readily with the $[Co^ISalen]^-$ anions to give the stable organometallic compound[3,4], the active particles formed prior to the substrate addition are thus excluded from the catalytic cycle.

The rate of reduction would not be great or the reaction proceed so far to completion if the final reaction product, *i.e.*, the dichloride, were able to compete effectively with the initial trichloride for the $[Co^ISalen]^-$ anions. Experiments involving addition of CH_3CHCl_2 to the system during the reduction of CH_3CCl_3 clearly indicated that the former is the less successful. In addition, if polarographic reduction of CoSalen is undertaken in the presence of chloroform and methylene chloride (Fig.2), catalytic waves appear at the expected potentials (*vide infra*) for the generation of organometallics during the electrode processes

$$CHCl_2Co^{III}Salen \xrightarrow[-0.86\,V]{} Co^{II}Salen \xrightarrow[-1.10\,V]{} [Co^ISalen]^- \qquad (4)$$

$$CHCl_3$$

$$Co^{II}Salen \xrightleftharpoons[-1.10\,V]{} [Co^ISalen]^-$$

$$CH_2Cl_2 \qquad (5)$$

$$CH_2ClCo^{III}Salen \xleftarrow{-1.20\,V}$$

The second-order rate constants of the reactions of CH_2Cl_2, $CHCl_3$ and CH_3CCl_3 respectively with the $[Co^ISalen]^-$ anion *in* DMF at 25° as derived from the catalytic currents[5] are ca. $(1.2-2.4)\cdot 10^2$, $1.1\cdot 10^5$ and $3.2\cdot 10^5$ $M^{-1}\cdot sec^{-1}$. Thus the anion $[Co^ISalen]^-$ reacts with chloroform 450—900 times as fast as with methylene chloride. Chloroform, in turn, reacts somewhat slower than 1,1,1-trichloroethane. This result may be due to hydrogen bonding of $CHCl_3$ with the DMF solvent, this link being broken in the transition state of the reaction.
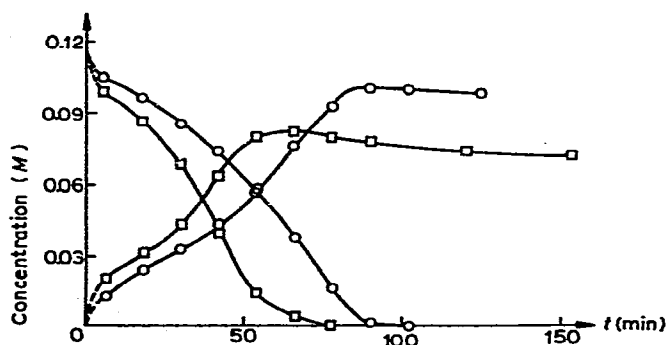

Fig.1. Kinetic curves for the reduction of *gem*-trichloroalkanes in terms of the disappearance of substrates (S) and appearance of the main products (P); DMF, 20°, $[S]_0 = 0.12\,M$, $[NaBH_4]_0 = 1.2\,M$, $[CoSalen]_0 = 1.2\cdot 10^{-3}\,M$. The solution of CoSalen and $NaBH_4$ was prepared 10 min before addition of the substrate. □, S = $CHCl_3$, P = CH_2Cl_2; ○, S = CH_3CCl_3, P = CH_3CHCl_2.
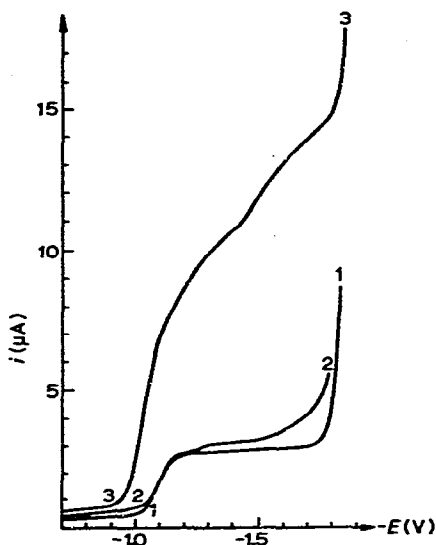
Fig.2. The effect of chloroform and methylene chloride on the polarographic reduction of CoSalen; 0.1 M solution of $NaClO_4$ in DMF as supporting electrolyte, $25°$. $t_1 = 1.0$ sec, $m = 1.3$ mg/sec, reference electrode, calomel/4 M aqueous LiCl. Curve 1, [CoSalen] $= 1.0 \cdot 10^{-3}$ M, Curve 2, [CoSalen] $= 1.0 \cdot 10^{-3}$ M, [CH_2Cl_2] $= 1.3 \cdot 10^{-3}$ M; Curve 3, [CoSalen] $= 1.0 \cdot 10^{-3}$ M, [$CHCl_3$] $= 1.3 \cdot 10^{-3}$ M.

Since the kinetic curves (Fig.1) retain an autocatalytic pattern up to high conversions it is reasonable to assume that the substrates are not involved in the rate-determining step. Hence the velocity of the catalytic reaction proper (eqns. 2, 3) must be limited by a reductive splitting of the Co—C bond (eqn. 3). If this is the case, the selectivity of catalysis toward the CCl_3 group must finally depend on the relative rates with which borohydride reduces the organometallics derived from tri- and dichlorides, i.e. $RCCl_2$CoSalen and RCHClCoSalen. The polarographic data indicate the former to be reduced much more readily: $E_{1/2} = -0.86$ and -1.20 V for $CHCl_2$CoSalen and CH_2ClCoSalen* respectively.

At present many low-spin cobalt complexes are known to form organic derivatives containing metal—carbon σ-bond[6]. The results reported in this communication suggest that the reduction of organic halides and related compounds in the presence of such cobalt complexes depends both on the formation of such organometallic entities and on their reactivity toward the reducing agent employed.

REFERENCES

1 D. Konrád and A. Vlček, *Proc. Symp. Coord. Chem., Tihany (Hungary), 1964*, Budapest, 1965, p. 265.
2 S.N. Zelenin and M.L. Khidekel, *Uspekhi Khim.*, 39 (1970) 209.
3 C. Floriani, M. Pupis and F. Calderazzo, *J. Organometal. Chem.*, 12 (1968) 209.
4 G.N. Schrauzer and E. Deutsch, *J. Amer. Chem; Soc.*, 91 (1969) 3341.
5 J. Heyrovský and J. Kůta, *Principles of Polarography*, Publ. House Czechoslovak. Acad. Sci., Prague, 1965, p. 383.
6 G. Costa, *Vortragsber. Symp. Koordinationschemie der Übergangselemente*, Jena, 1969, Sect. C, S. 27.

*These compounds were obtained as monohydrates from an application of the procedure of Floriani et al.[3] for the synthesis of CoSalen alkyl derivatives.