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The Effect of Crown Ethers on the Reaction of Alkali Metal Trichloroacetate with Cyclohexene under Decarboxylative Conditions

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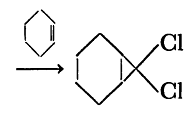
Synopsis. The reaction between alkali metal trichloroacetate and cyclohexene was studied in an aprotic medium in the presence and also in the absence of crown ethers. The crown ethers catalyzed decarboxylation but reduced the yield of the dichlorocarbene adduct.

Since the discovery of crown ethers and their metal complexes, numerous applications in organic chemistry have been worked out, in particular on the activation of anionic species as regards synthetic problems.[1] The anionic activation through complexation of alkali metal cations by crown ethers has been confirmed by the enhancement of nucleophilicity and basicity. However, recent studies show a variation of anionic activation, in which decarboxylation of certain alkali metal carboxylates is greatly accelerated. Hunter *et al.*[2] decarboxylated sodium 3-(9-fluorenylidene)-2-phenylacrylate in THF in the presence of dibenzo-18-crown-6 (I), and Smid *et al.*[3] described the decarboxylative rearrangement of potassium 6-nitrobenzisoxazole-3-carboxylate in aqueous media under the catalysis of a polymer crown, poly(vinylbenzo-18-crown-6). These works prompted us to examine the catalytic effect of crown ethers on the decarboxylation of alkali metal trichloroacetates, which has a synthetic utility to generate dichlorocarbene under neutral conditions.[4,5]

Results and Discussion

The reaction of alkali metal trichloroacetate with cyclohexene under decarboxylative conditions (Eq. 1) was studied in a suspension or solution in aprotic solvent using a thermostatted cell fitted with a small reflux condenser at 50—80 °C with and without added crown ether. The reaction was monitored by measuring the volume of evolved gas and analyzing the reaction mixture directly on GLC for 7,7-dichloronorcarane. In a typical run, 1.0 g of trichloroacetate salt, 2.6 g of cyclohexene (a large excess), 10 ml of appropriate solvent and 5—20 mol% (based on the salt) of crown ether (I, benzo-15-crown-5 (II) and dicyclohexyl-18-crown-6(III)) were utilized under anhydrous conditions. After the salt had been dried in the thermostatted cell under reduced pressure for 30 min, cyclohexene and the solvent were introduced into the cell, which was then connected to a gas burette, and the mixture was vigourously stirred magnetically. Crown ether dissolved in a solvent was used.

$$\mathrm{CCl_3COOM} \xrightarrow[\Delta]{-\mathrm{CO_2}} \mathrm{CCl_3M} \xrightarrow{-\mathrm{MCl}} :\mathrm{CCl_2}$$



(M=Li, Na, K) (1)

Reaction in the Absence of Crown Ether. The decarboxylation of potassium trichloroacetate at 80 °C was almost complete (>90% of the theoretical amount according to Eq. 1) within 30 min in acetonitrile and 1,2-dimethoxyethane (DME), while in benzene only 20% decarboxylation was observed after 5 h. As a solvent acetonitrile was at least four times more effective than DME when the reaction was carried out at 70 °C. Sulfolane behaved similarly to acetonitrile. The formation of dichloronorcarane paralleled the time course of the decarboxylation, but the yield remained at ≈50% after 30 min (and for the rest of the reaction time) in acetonitrile and DME, and only at 2% (or 10% based on the salt decomposed) after 5 h in benzene. While the former yields are comparable to those originally reported by Wagner for the sodium salt in DME,[4] the extremely low yield in benzene is obviously caused by the insolubility of the salt, where decarboxylation took place in the suspended solid. The effect of cations (Li^+, Na^+, K^+) studied in acetonitrile (70 °C) and DME (80 °C)* showed that the initial rate of decarboxylation and the carbene adduct formation were in the increasing order of $K^+>Na^+>Li^+$ in line with previous results.[5] A difference of several times the magnitude of rates was observed between adjacent cations. Decomposition is accelerated when the anion is less tightly bound to cations of larger ionic radius. The enhanced reactivity in acetonitrile as compared with DME is also in line with the medium effect expected on the structure of ion pairs in aprotic medium.[2] However, it was noticeable that the final yield in the adduct was not proportional to the ease of decarboxylation. As an example, lithium salt in acetonitrile at 70 °C attained 80% decarboxylation and 60% yield of 7,7-dichloronorcarane in 5 h, and the reaction was still in progress. On the other hand, the reaction was complete for potassium and sodium salts well within a half hour, but the yields of the carbene adduct were 52 and 55% respectively.

Effect of Crown Ethers. The effect of added crown ethers in acetonitrile or DME was found to proceed in two ways, *i.e.*, a rate acceleration (both in decarboxylation and carbene adduct formation) and a decrease in the final yield of the carbene adduct. The rate increase in the initial phase of the reaction in the presence of 20 mol % of II ranged from two to

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* Solubility of the salts in the solvents was in the order Li>Na>K. Lithium and sodium salts essentially gave uniform solutions.

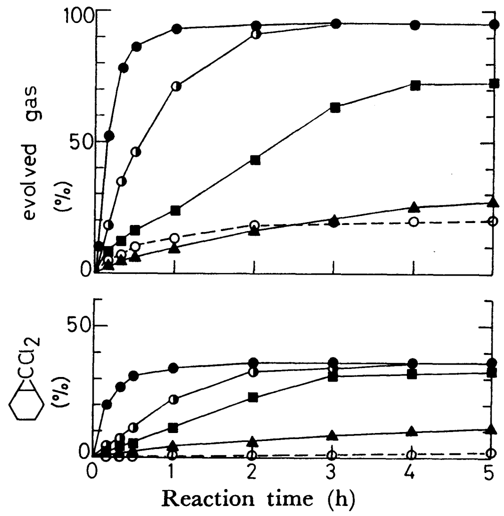

Fig. 1. Decarboxylation of potassium trichloroacetate in benzene (80 °C). Benzene, 10 ml; cyclohexene, 2.6 g; CCl_3CO_2K, 1.0 g(5.0 mmol). —▲— I(0.3 mmol); —■— II(1.0 mmol); —●— III(1.0 mmol); —◑— III(1.0 mmol), without benzene, cyclohexane 10 ml; --○-- without crown ether.

nine times of that in the case of its absence depending on the cation and the solvent. The rate increase was sufficient to lower the practical reaction temperature by 10—20 °C. However, the advantage was counterbalanced by the decrease in the yield of the adduct to two thirds of those in the case of the absence of crown ethers. The effect of crown ethers in benzene was much more pronounced. On addition of 20 mol % of III the reaction effectively approximated that in DME, as shown in Fig. 1. Even the reaction in cyclohexene (as both reactant and solvent) was successful. Obviously the crown ethers functioned as a solid-liquid phase-transfer catalyst.[1] In line with a similar observation on the effect of alkali metal ions, the trichloroacetate ion which is less tightly bound to the cation or freed from the cation by the intervention of crown ether decarboxylates more readily, but it introduces some unfavorable effects on the subsequent carbene formation and its reaction to form the adduct. The exact nature of these effects is not clear at present in view of the complexity of the side reactions involved in the carbene-generating system.[5,6] Decarboxylation on alkali metal trichloroacetate in aprotic medium was accelerated considerably by the cation complexation with crown ethers, but the extent was far less than the cases in which the resulting anions were strongly resonance-stabilized.[2,3,7,8] The acceleration of decarboxylation was counterbalanced by the reduced yield of dichlorocarbene adduct, thus diminishing the synthetic utility of crown ethers in the system.

References

1) G. W. Gokel and H. D. Durst, *Synthesis*, **1976**, 168.

2) D. H. Hunter, W. Lee, and S. K. Sim, *J. Chem. Soc., Chem. Commun.*, **1974**, 1018.

3) J. Smid, S. Shah, L. Wong, and J. Hurley, *J. Am. Chem. Soc.*, **97**, 5932 (1975).

4) W. M. Wagner, *Proc. Chem. Soc., London*, **1959**, 229.

5) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y. (1971), p. 137.

6) E. V. Dehmlow, *Tetrahedron Lett.*, **1976**, 91, and the literature cited therein.

7) D. S. Kemp and K. G. Paul, *J. Am. Chem. Soc.*, **97**, 7305 (1975).

8) D. S. Kemp, D. D. Cox, and K. G. Paul, *J. Am. Chem. Soc.*, **97**, 7312 (1975).