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The Thermal Decomposition of Carbonates to Ethers

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The thermal decomposition of a wide range of compounds proceeds via a cyclic transition state (Figure 1).[1] Such compounds include acetates,[1] phenylacetates,[2] benzoates,[3] carbamates,[4] carbonates,[5-7] chloroformates,[8‡] and cyanoformates.[9]

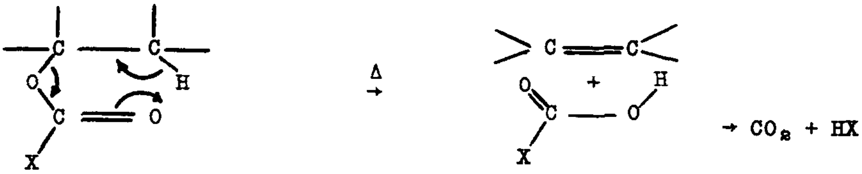

Figure 1 (X = Me, $PhCH_2$, Ph, NR_2, OR, Cl, CN)

For cyanoformates,[9] chloroformates,[8,10] and carbamates,[11] a series along which electron withdrawal by X decreases, an alternative decomposition has been reported to accompany that given above with a decreasing extent along the series. This produces carbon dioxide and respectively, alkyl cyanide, alkyl chloride, or alkyl amine. The reaction is surface catalysed and tends to become an increasingly important side reaction the lower the temperature (so that its activation energy is lower than for the reaction given by Figure 1).

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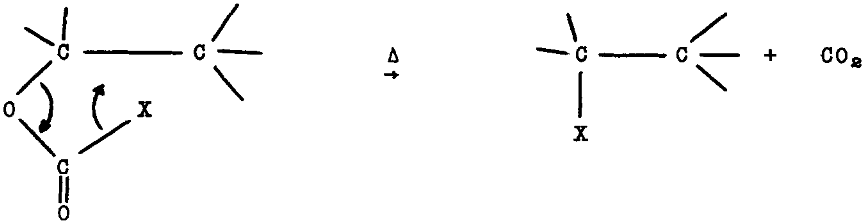
‡ For chloroformates the transition state originally proposed differed from that shown, chlorine and the carbonyl oxygen being interchanged. In the light of the common mechanism now known to apply to the other compounds, this proposal is probably incorrect.

The reaction most probably proceeds *via* the 4-centre S_Ni process, Figure 2, and this should be more rapid the more electron withdrawing is X. This mechanism has been proposed to account for the thermal decomposition of chlorosulphites to alkyl chlorides and sulphur dioxide[12] and of aryl fluoroformates to aryl fluorides; the latter is also surface catalysed.[13] The decomposition of chlorosulphites shows a secondary β-deuterium isotope effect[14] which suggests carbonium ion intermediacy so that in the transition state the carbon-oxygen bond breakage is insufficiently compensated by carbon-X bond formation.



(X = CN, Cl or NR_2)

Figure 2

It follows that carbonates (X = OR) should also undergo this elimination quite readily and the lack of any report of it suggests that the structure of carbonates renders them less susceptible to surface-catalysed decomposition. We now describe conditions under which this reaction takes place.

Ethyl phenyl carbonate was heated at *ca.* 175° in a glass vessel during 7 days. Analysis of the products by g.l.c.-linked mass spectrometry showed only the formation (in *ca.* 20% yield) of the expected phenol. In the presence of palladium on charcoal however both phenetole (Figure 2, X = OPh) and phenol were formed in *ca.* 2:1 ratio and 25% yield; these results could be qualitatively duplicated. By contrast heating ethyl *p*-nitrophenyl carbonate at approximately the same temperature even without an added active surface produced *p*-nitrophenetole as the major reaction product in *ca.* 75% yield, *p*-nitrophenol (10%) being also obtained as expected. At higher temperatures (*ca.* 450°), *p*-nitrophenol was effectively the sole reaction product, only traces of *p*-nitrophenetole being produced. The reaction producing the latter therefore has the lower activation energy confirming the analogy with the other reactions. It is possible that under the conditions used for kinetic studies of the decomposition of aryl ethyl carbonates to phenols (363°),[6] some nitrophenetoles may have been produced from the nitro isomers since there was an indication of a secondary decomposition.[6] However no *p*-nitrophenetole could be detected on decomposing the *p*-nitro isomer under the same kinetic conditions which may reflect the deactivated surface of the kinetic reactor employed [Many nitroaromatics appear to be unstable at elevated temperatures (*eg*. nitrostyrenes) and kinetic studies with these are usually accompanied by secondary decomposition]. Quite strongly electron-withdrawing groups X are evidently required to produce ether formation (and indeed the S_Ni reaction in general) so that for example ethyl *m*-chlorophenyl carbonate is reported to produce only *m*-chlorophenol on heating.[15]

Competition between this gas-phase S_Ni reaction and elimination shows parallels with nucleophilic substitution and elimination in solution. In both cases substitution is favoured by lower temperature and in solution, substitution (involving pseudo pentacoordinate carbon) is retarded by steric hindrance at the α-carbon atom. For carbamates[2] the extent of the S_Ni reaction diminishes along the series 1°>2°>3° which suggests that in the gas phase too, steric hindrance is the factor responsible. Some indication that the same is true for carbonates comes from the palladium/charcoal-catalysed decomposition of t-butyl phenyl carbonate (175°, 6h); phenol and t-butyl phenyl ether were both produced but here the former was the dominant product.

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