Electron Impact Studies. Part 143.† An Ion Cyclotron Resonance Study of the Gas-phase Reactions of Alkoxide Ions with Dialkyl Carbonates

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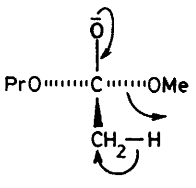
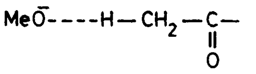
The reaction between an alkoxide ion R^1O^- and a dialkyl carbonate $(R^2O)_2CO$ produces the product ions $R^1OCO_2^-$ and $R^2OCO_2^-$. The former ion is produced by nucleophilic attack of R^1O^- at the carbonyl centre of the dialkyl carbonate, whereas the latter ion is produced by attack of alkoxide ions at both the carbonyl centre and at an alkyl group R^2. The results obtained from ^2H- and ^{18}O-labelling studies suggest that the decomposing species formed during nucleophilic addition to the carbonyl centre has a tetrahedral structure. No stable species corresponding to $[R^1O^- + (R^2O)_2CO]$ is observed. The extent of nucleophilic attack at the carbonyl centre (compared with that at the alkyl group R^2) decreases with elaboration of the alkyl groups R^1 or R^2.

THE elucidation of the structures of both stable and decomposing adducts formed in gas-phase nucleophilic substitution reactions at *sp*²-carbon has been the aim of a number of recent investigations.[1-10]

Theoretical calculations suggest that the stable adducts detected during the reactions of alkoxide negative ions with ketones [7] and esters [9] may have tetrahedral structures (*e.g. a*).[10] The corresponding hydrogen-bound association complexes (*e.g. b*), or the 'tetrahedral-like' association complexes that look like products or reactants are thermodynamically less stable than the tetrahedral structure in these cases.[10] In contrast, for reactions between nucleophiles and acid halides, kinetic evidence suggests that the tetrahedral structure is a transition state rather than a reactive intermediate.[4]



a

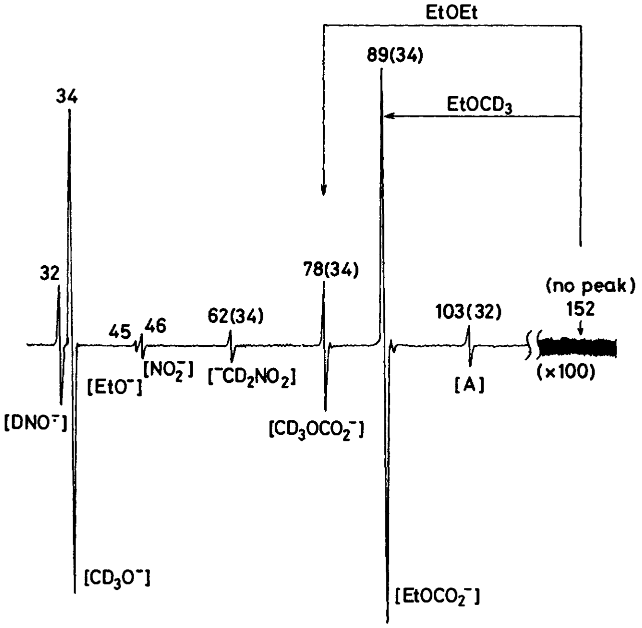


b

Simple esters undergo a variety of reactions with alkoxide negative ions, one of which involves reaction through the decomposing species *a* (shown for the specific case of PrO^-–$MeCO_2Me$).[9] The decomposing species formed in the AcO^-–Ac_2O system is also thought to have a tetrahedral structure.[2,7]

RESULTS AND DISCUSSION

We describe here the reactions of dialkyl carbonates with alkoxide and 'solvated' alkoxide ions. We specifically chose to study the carbonate system $(R^2O)_2CO$ because (i) it should undergo facile nucleophilic displacement with an alkoxide ion to yield an ion $R^2OCO_2^-$ and (ii) nucleophilic attack at the carbonyl carbon may produce a decomposing species of tetrahedral geometry containing both a plane and C(2) axis of symmetry. The intermediacy of such a species may be inferred if there is an appropriate decomposition channel available which may be used to demonstrate the symmetry of the decomposing system.



Negative-ion i.c.r. spectrum of the system CD_3ONO–$(EtO)_2CO$. Experimental conditions as stated in Experimental section. Values in parentheses define the mass of the precursor ion, as measured by cyclotron ejection. The ion designated [A] is formed by the process

$$(EtO)_2CO + DNO^{\bullet -} \rightarrow [EtO{\cdot}CO{\cdot}NO]^{\bullet -} + EtOD$$ (*cf.* ref. 9).

This is a standard reaction of esters and occurs when all neutral species listed in the Table are allowed to react with $DNO^{\bullet -}$ (from CD_3ONO)

The spectrum obtained from the reaction between CD_3O^- and diethyl carbonate is shown in the Figure. The basic features of this spectrum may be summarised as follows: (i) no stable adduct corresponding to $[(EtO)_2CO + CD_3O^-]$ is detected; (ii) the formation of EtO^- by nucleophilic attack of CD_3O^- at the carbonyl carbon is a very minor process; (iii) the peak corresponding to $CD_3OCO_2^-$ must be formed by nucleophilic attack of CD_3O^- at the carbonyl centre (perhaps to form *c*) followed by elimination of the elements of diethyl ether [reaction (A1)]; (iv) the major peak in the spectrum

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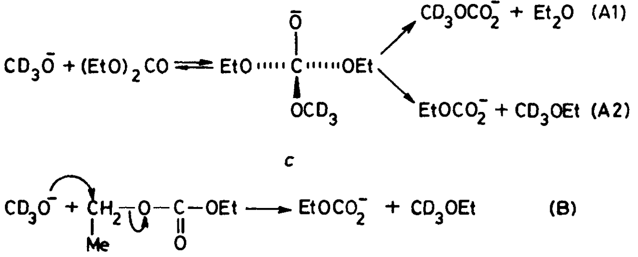
corresponds to $EtOCO_2^-$. The large abundance of this peak suggests the possibility that it may be formed by the S_N2 process (B) as well as by reaction (A2).



A number of questions arise from a consideration of the Figure. (1) What are the relative proportions of product ions formed by reactions (A) and (B)? (2) Can we confirm that reaction (A) proceeds through the tetrahedral species *c*? (3) Is it possible to detect stable adducts corresponding to *c*? (4) If reaction (A) proceeds through *c*, what is the intimate mechanism by which *c* decomposes to yield product ions? In order to answer these questions we have carried out a number of experiments, the majority of which are summarised in the Table.

Ion–molecule products formed by reaction between alkoxide ions and dialkyl carbonates [a]

Neutral $R^2O–C(=O)–OR^{2'}$						
R^2	$R^{2'}$	Attacking alkoxide (R^1O^-) (abundance)	$R^{2'}O^-$	$MeOCO_2^-$	$CD_3OCO_2^-$	$R^2OCO_2^-$ when R^2 = Et or Pr
Me	Me	MeO^- (75)	[b]	100		
Me	Me	CD_3O^- (81)		100	29	
Me	CD_3	CD_3O^- (85)	[b]	63	100	
CD_3	CD_3	$Me^{18}O^-$ [c]		[d]	[e]	
Me	Me	EtO^- (68)		100		12
Me	CD_3	EtO^- (100)		80	80	16.5
Me	Et	MeO^- (78)	1	100		35
Me	Et	CD_3O^- (85)	1	100	43	52
Me	Me	PrO^- (90)		100		6
Me	CD_3	PrO^- (100)		75	75	9
Me	Pr	MeO^- (82)	3	100		18
Me	Pr	CD_3O^- (88)	4	100	35	24
Me	Me	Pr^iO^- (85)		100		3
Me	CD_3	Pr^iO^- (100)		85	85	5
Me	Me	Bu^tO^- (76)		100		
Et	Et	MeO^- (80)	2	17		100
Et	Et	CD_3O^- (85)	2		23	100
Et	Et	EtO^- (73)	[b]			100
Pr	Pr	MeO^- (92)	6	15		100

[a] Experimental conditions—see Experimental section. For a complete spectrum see the Figure. [b] $R^1 = R^{2(')}$ [c] $Me^{18}O^-$ (^{18}O 20.5%, $^{16}O^-$ 79.5%), total abundance of $Me^{16}O^-$ and $Me^{18}O^-$ 90% (for comparison with other examples listed in Table 1). [d] Total abundance of $Me^{16}OCO_2^-$ and $Me^{18}OCO_2^-$ peaks 30%. Ratio of two peaks 4 : 1, *i.e.* full retention of label. [e] Total abundance of $CD_3{}^{16}OCO_2$ and $CD_3{}^{18}OCO_2^-$ peaks 100%. Ratio of two peaks 100 : 6.5.

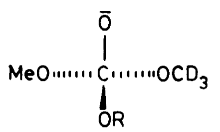
The Question of the Formation of Stable Adducts.—*Ab initio* LCAO-MO-SCF calculations have been used to determine the stabilities of various types of possible adducts formed between alkoxide ions and carbonyl-containing systems.[10,11] The reaction between HO^- and H_2CO_3 is prototypical of the systems used in this study, and the energy-optimised structures of HO^-, H_2CO_3, and the tetrahedral adduct $H_3CO_4^-$ have been determined by cycles of geometric variation through Gaussian 76 with STO 3G bases.[12] These calculations indicate that tetrahedral $H_3CO_4^-$ is a stable species (ΔH_f −234 kJ mol^{-1}). This suggests that the species *c* could indeed be a reactive intermediate in reaction (A), and that it may be possible to detect such an ion in an i.c.r. experiment.

Stable adducts $[R^1O^- + (R^2O)_2CO]$ are *not* detected for those systems listed in the Table. Cell pressures of 2×10^{-5} Torr were used for these experiments. Stable adducts are not detected even when the cell pressure is increased to 10^{-4} Torr, *i.e.* under conditions where collisional stabilization of an adduct may occur. A method which has been used to effect the stabilization of such intermediates utilizes the reaction between a 'solvated' alkoxide ion $[(R^1O^- \cdots HOR^1)$, produced by reaction of R^1O^- with $HCO_2R^1]$ and the appropriate carbonyl compound. The molecule of R^1OH which is eliminated acts as an energy sink for the reaction.[1,8,13] The reactions between such species and dialkyl carbonates do *not* produce detectable intermediates $[(R^2O)_2CO + R^1O^-]$, in marked contrast to the pronounced adducts formed in the analogous reaction with simple esters.[11] It must be concluded that the formation of the product ions $R^1OCO_2^-$ and $R^2OCO_2^-$ is so facile as to preclude the detection of a tetrahedral species *c* on the time scale used for these experiments.

The Structure of the Decomposing Species in Reaction (A).—An examination of the data in the Table shows that ions $R^2OCO_2^-$ formed from $(R^2O)_2CO$ and R^1O^- arise both by nucleophilic attack at an alkyl carbon [reaction type (B)] and at a carbonyl carbon [reaction type (A)].

The relative extent to which these processes occur for different systems will be considered later. It is sufficient to state at this stage that nucleophilic attack at carbonyl is a significant process when R^1 and R^2 = Me or Et.

If an alkoxide ion R^1O^- undergoes reaction with MeO–C(O)–OCD_3 then the product ions $MeOCO_2^-$ and $CD_3OCO_2^-$ should be formed in equal amounts if (i) there is no secondary isotope effect operating for process (B), and (ii) if nucleophilic attack of R^1O^- at the carbonyl centre produces an intermediate (*e.g. d*) which eliminates CD_3OR and MeOR to an equal extent. The data listed in the Table show that the reactions of EtO^-, PrO^-, and Pr^iO^- with MeO–C(O)–OCD_3 give the product ions $MeOCO_2^-$ and $CD_3OCO_2^-$ in exactly equal amounts. Reaction (A) therefore occurs through a symmetrical decomposing ion and there is a high probability that that ion has a tetrahedral structure.



d

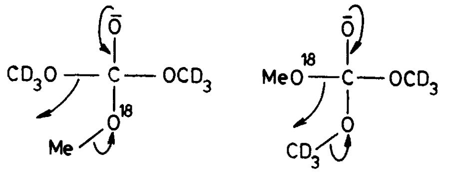
The Relative Extents of the Competing Nucleophilic Reactions (*A*) *and* (*B*).—The relative proportions of ion $MeOCO_2^-$ formed by processes of the types (A) and (B) for the system MeO^-–$(MeO)_2CO$ may be determined by deuterium labelling studies, since it has already been shown that there are no detectable secondary isotope effects operating for such reactions when a methyl group is replaced by CD_3. The systems CD_3O^-–$(MeO)_2CO$ and CD_3O^-–$CD_3OC(O)OMe$ show product ions $MeOCO_2^-$ and $CD_3OCO_2^-$ in the respective ratios 100 : 29 and 63 : 100. A combination of reaction types (A) (70%) and (B) (30%) give theoretical ratios of 100 : 30 and 61 : 100 for the product ions $MeOCO_2^-$ and $CD_3OCO_2^-$ in the two systems described.

Approximately 70% of $MeOCO_2^-$ ions formed in the reaction between MeO^- and $(MeO)_2CO$ (under the stated experimental conditions) are thus formed by nucleophilic attack at the carbonyl centre [reaction type (A)]. Similarly, deuterium labelling shows that nucleophilic attack at the carbonyl centre produces 60 and 52% of the product ions $MeOCO_2^-$ for the respective systems MeO^-–MeOC(O)OEt and MeO^-–MeOC(O)OPr (see Table).

As a general rule, the extent of nucleophilic attack at the carbonyl centre decreases (with respect to nucleophilic attack at an alkyl carbon) with increasing size of the alkyl groups on either the carbonate or the attacking nucleophile. In the extreme case of the system Bu^tO^-–$(MeO)_2CO$, the expected peak corresponding to the ion $Bu^tOCO_2^-$ is not observed (see Table).

The Decomposition Mechanism of the Symmetrical Intermediate.—The decomposing intermediate in a reaction of type (A) eliminates a dialkyl ether. It is not clear however which of the oxygen atoms is lost during this reaction. In order to clarify this question, we studied the system $Me^{18}O^-$–$(CD_3O)_2CO$ which should produce the decomposing species *e*.

The spectrum derived from $Me^{18}O^-$ and $(CD_3O)_2CO$ shows that the $Me^{18}OCO_2^-$ ion has retained all the ^{18}O label. In addition, peaks corresponding to $CD_3OCO_2^-$ and $CD_3OC^{16}O_1{}^{18}O_1{}^-$ occur in the ratio 100 : (40 ± 5).* The theoretical ratio obtained on the assumptions that (i) 70% of the product ions are produced by nucleophilic attack at the carbonyl centre and (ii) ^{16}O and ^{18}O may be lost equally in the formation of product ions containing CD_3, is 100 : 44. Within experimental error, ^{16}O and ^{18}O are thus lost equally, *i.e.* the eliminations shown in *e* and *f* occur to an equal extent.



e

In summary, we have shown: (i) that an alkoxide ion R^1O^- may react at both alkyl and carbonyl centres of a dialkyl carbonate $(R^2O)_2CO$, (ii) that there is a high probability that nucleophilic addition to the carbonyl centre yields a decomposing species of tetrahedral geometry, and (iii) that increasing the size of either of the alkyl groups R^1 or R^2 decreases the extent of nucleophilic addition of R^1O^- to the carbonyl centre when compared with that of the S_N2 reaction at R^2.

EXPERIMENTAL

I.c.r. spectra were measured with a Dynaspec ICR9 spectrometer equipped with a three-section cell. Spectra can either be obtained in the 0—5 eV range (primary negative ions formed by dissociative thermal electron capture) or in the range 40—80 eV (primary negative ions formed by dissociative secondary electron capture). The latter range gives the better sensitivity, hence spectra were obtained routinely at a nominal 70 eV. Other reaction conditions: $\omega/2\pi$ 125.0 kHz, R^1ONO pressure 5×10^{-6} Torr, total pressure 2×10^{-5} Torr, ion current of the order of 10^{-10} A, emission current 0.2 μA, and ion transit time 1×10^{-3} s. Precursor ions in reaction sequences were determined by the cyclotron ejection technique.

Those experiments which utilized 'solvated' alkoxide ions [RO^- . . . HOR] were carried out by the method of Riveros.[1] Partial pressures of components were as follows: R^1ONO (5×10^{-6} Torr), HCO_2R^1 (1×10^{-5} Torr), and $(R^2O)_2CO$ (1×10^{-5} Torr). The following systems were studied: MeONO–HCO_2Me–$(MeO)_2CO$, MeONO–HCO_2Me–$(EtO)_2CO$, and EtONO–HCO_2Et–$(MeO)_2CO$. Peaks due to adducts [R^1O^- + $(R^2O)_2CO$] were neither observed under the above conditions, nor when the total cell pressure was increased to 2×10^{-4} Torr.

Alkyl nitrites were prepared on the day of the i.c.r.

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* $Me^{18}O^-$ used in this experiment had ^{16}O 80 and ^{18}O 20%. The ratio of 100 : (40 ± 5) is that which would be obtained using $Me^{18}O^-$ (^{18}O 100%); the actual ratio has been adjusted to give the figure for $Me^{18}O^-$ (^{18}O 100%).

experiment. Methyl, [$^2H_3$]methyl, ethyl, propyl, isopropyl, and t-butyl nitrite were prepared by a reported method[14] from the appropriate alcohol and sodium nitrite. Methyl [^{18}O]nitrite ($Me^{18}ONO$, ^{18}O 20.5%) was prepared from [^{18}O]methanol[15] by the standard method.[14]

Dimethyl and diethyl carbonates were purified commercial samples. Di-n-propyl, methyl [$^2H_3$]methyl ($^2H_3$ 100%), methyl propyl, ethyl methyl, [$^2H_5$]ethyl methyl ($^2H_5$ 100%), and methyl t-butyl carbonate were prepared from the appropriate alcohol and chloroalkyl formate by a general procedure.[16] [$^2H_6$]Dimethyl carbonate ($^2H_6$ 100%) was prepared by the procedure of Röse.[17] All dialkylcarbonates were purified by preparative g.l.c. using an OV 101 (15%), 6 m × 6 mm column.

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