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Loss of CO_2 from the *ortho* isomer of deprotonated methyl phenyl carbonate involves a methyl migration

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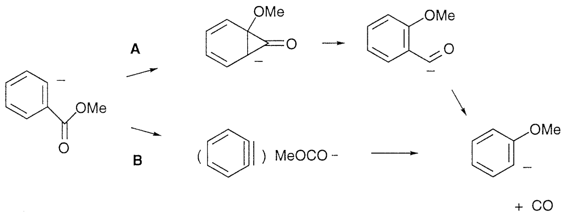
Abstract

The collision induced decompositions of the *ortho-*, *meta*, and *para-* $(M - H)^-$ anions of methyl phenyl carbonate were studied to see whether there is loss of CO_2 occurring by the benzyne cine-substitution $\{(C_6H_4)^- - OCO_2Me \rightarrow [(C_6H_4)MeOCO_2^-] \rightarrow (C_6H_4)^- - OMe + CO_2\}$. Loss of CO_2 is observed from the *ortho* isomer, but the process does not involve a benzyne cine substitution. It is a methyl migration through a six-centre transition state to give a cresol $(M - H)^-$ ion, probably *ortho*-$MeC_6H_4 - O^-$. Theoretical calculations [at the B3LYP/6-311++G(*d,p*)//HF/3-21+G(*d*) level of theory] indicate the methyl migration is a stepwise process, with the barrier for the first (and rate determining) step being 191 kJ mol^{-1}. The overall process is calculated to be exothermic by 276 kJ mol^{-1}. (Int J Mass Spectrom 210/211 (2001) 557–562) © 2001 Elsevier Science B.V.

Keywords: Deprotonated methyl phenyl carbonate; Negative ions; Rearrangement

1. Introduction

We have recently reported that the collision-induced loss of carbon monoxide from deprotonated methyl benzoate is a charged-induced reaction [1]. Carbon monoxide is lost from deprotonated methyl benzoates with anion sites in the *ortho-*, *meta-*, and *para-*positions in the ratio $o > m \gg p$, and it has been proposed that this is due to 1,2-H rearrangements on the phenyl ring yielding the *ortho* anion, the species that eliminates carbon monoxide. The mechanism for loss of CO is suggested to be one of the two possibilities shown in Scheme 1. The cyclisation process has a barrier of 199 kJ mol^{-1} [at the B3LYP/6-311++G(*d,p*)//HF/6−31+G(*d*) level of theory] for rate determining step **A** compared with a barrier of 281 kJ mol^{-1} for rate determining step **B** of the benzyne cine-substitution process. However, step **B** has a higher Arrhenius pre-exponential factor than step **A**, so it is not possible to say which of the two mechanisms is the more favoured kinetically. The



Scheme 1.

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This paper is dedicated to Professor Nico M.M. Nibbering, an excellent colleague and friend over all the years.

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overall process is endothermic by some 85 kJ mol^{-1} at the level of theory of the calculation used [1]. This article describes the mechanism for the loss of CO_2 from deprotonated methyl phenyl carbonate: an analogous system.

2. Experimental

2.1. Synthetic procedures

Methyl phenyl carbonate and *o*-cresol were commercial samples and were used without further purification. The three isomeric methyl (trimethylsilylphenyl) carbonates were made reported methods [2–5].

2.2 Computational methods

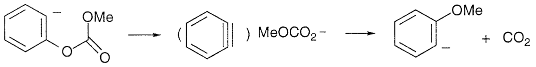
Geometry optimisations were carried out with the HF/3-21+G(*d*) level of GAUSSIAN 94 [6]. Energies were optimised at the Becke 3LYP method [7,8], i.e. B3LYP/6-311++G(*d*,*p*)//HF/3-21+G(*d*). The calculated frequencies were also used to determine the zero-point vibrational energies which were then scaled by 0.9207 [9] and used as a zero-point energy correction for the electronic energies calculated at the higher level of theory. Stationary points were characterised as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. Calculations were carried out using the Beowulf computing cluster at the South Australian Computational Chemistry Facility (The University of Adelaide).

2.3 Mass spectrometric methods

Collisional activation mass spectra (CA MS/MS) were measured using a two-sector reversed geometry VG ZAB 2HF spectrometer. This instrument and the typical experimental conditions of negative ion chemical ionisation (NICI) have been described in detail elsewhere [10]. Samples were introduced into the source by way of a heated septum inlet, producing a measured pressure of 5×10^{-6} Torr inside the source housing. Typical ionization conditions were; source temperature, 200 °C; ionising energy, 70 eV (tungsten filament); accelerating voltage, −7 kV. All slits were fully open in order to minimize mass discrimination effects due to energy resolution [11]. The reagent ion HO^- was generated from electron impact on H_2O (introduced through the heated septum inlet to give an operating pressure inside the source housing of $\sim 5 \times 10^{-5}$ Torr, and thus an estimated pressure inside the ion source of close to 0.1 Torr). Negative ion chemical ionisation of the sample either effected deprotonation, or desilylation of a neutral trimethylsilylated substrate, by analogy to the method originally developed by DePuy and co-workers [12]. Collisional activation (CA) spectra were obtained by collision of the incident anions with argon in the first of two collision cells at a pressure typically around 10^{-7} Torr. This reduces the main beam to 90% of its initial value, producing essentially single collision conditions in the collision cell [13]. Charge reversal (CR) [14,15] spectra were determined as for CA spectra except that the voltage of the electric sector is reversed in order to allow the passage of positive ions.

3. Results and discussion

The benzyne process is the simpler of the two processes shown in Scheme 1: this is the mechanism we favour even though there is no conclusive evidence to support such a view. We have tried to construct a system in which an analogous benzyne-anion complex should lead to a cine-substitution product by a reaction more kinetically and thermodynamically favourable than the benzyne process shown in Scheme 1. The process we decided to investigate was the cognate reaction of deprotonated methyl phenyl carbonate shown in Scheme 2. Not only



Scheme 2.

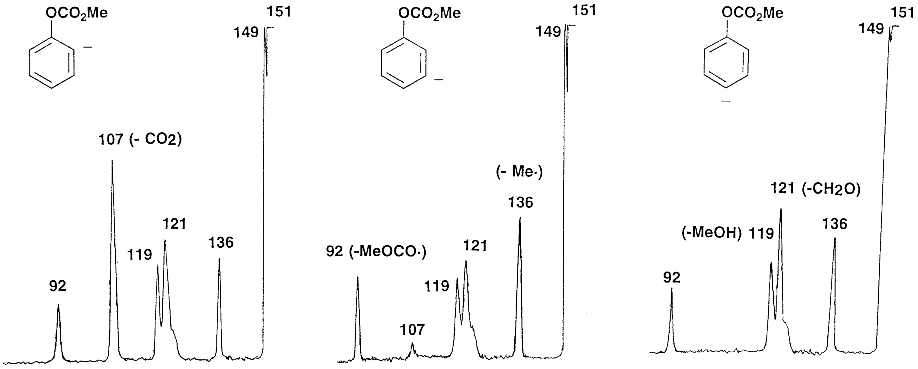


Fig. 1. Collisional activation mass spectra (MS/MS) of the *ortho*-, *meta*-, and *para*-anions of methyl phenyl carbonate, formed by the respective $S_N2(Si)$ reactions between HO^- and the appropriate methyl (trimethylsilylphenyl) carbonate. VGZAB 2HF mass spectrometer. For experimental conditions see Sec. 2.

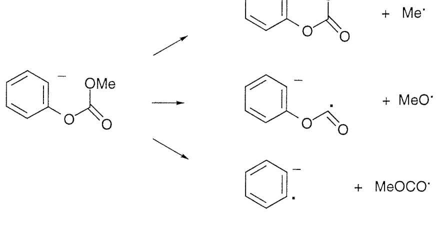
should $MeOCO_2^-$ be a good MeO^- donor, but the loss of CO_2 (rather than CO) makes the overall reaction endothermic by only 6 kJ mol^{-1} [compared with 85 kJ mol^{-1} for the comparable reaction of $(C_6H_4)^- - CO_2Me)$] [16]. There is also of course the possibility of an analogous cyclisation process similar to route **A** of Scheme 1.

Thus we prepared the three methyl (*ortho*-, *meta*-, and *para*-trimethylsilylphenyl) carbonate isomers and used the standard $S_N2(Si)$ reactions [12,17] between these neutrals and HO^- to produce the *ortho*-, *meta*-, and *para*-anions of methyl phenyl carbonate. The collisional activation spectra of these isomeric anions are shown in Fig. 1.

The spectra shown in Fig. 1 are much more complex than those of the analogous three methyl benzoate anions. The loss of CO_2 is only predominant in the spectrum of the *ortho*-isomer a result quite different to that observed for the losses of CO from the methyl benzoate anions (which are observed in the spectra of all the methyl benzoate anions). Most unusual however are the losses of Me•, CH_2O, MeO•, MeOH, and MeOCO•, where the relative abundances of these product peaks are comparable for all the spectra shown in Fig. 1: i.e. the processes appear to occur independently of the position of the anion centre on the phenyl ring. This must mean that these losses are either charge-remote and thus independent of and uninfluenced by the position of the anion centre on the ring, and/or they are anion-directed fragmentations which occur after equilibration of the carbanion centres on the phenyl ring [e.g. by successive 1,2-H transfers of the type which were proposed for the cognate methyl benzoate anion centres, processes which have barriers near 260 kJ mol^{-1} (calculated at the B3LYP/6-311++G(*d,p*)//HF/6-31(*d*) level of theory)] [1].

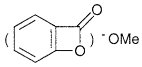
The processes involving radical losses are almost certainly charge-remote processes. We have shown using 1,3-disubstituted adamantanes that ester groups ($-CO_2R$) when placed in a position where they cannot be influenced by the functionality containing the negative charge, fragment by the competitive losses of R•, RO•, and ROCO• to form distonic radical anions [18]. Thus we propose that the losses of Me•, MeO•, and MeOCO• observed in Fig. 1 are charge-remote radical cleavages as shown in Scheme 3 for the *ortho*-isomer. The last of these species, the *o*-benzyne radical anion has been studied by Squires and co-workers [19].

The losses of MeOH and CH_2O must either be



Scheme 3.

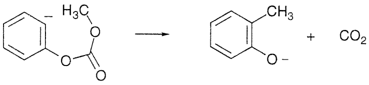
reactions of MeO· (charge-remote reactions) or MeO^- (charge-initiated reactions). Losses of MeOH and CH_2O are not observed from $^-CO_2Me$ groups in our studies of remote reactions using 1,3-disubstituted adamantancs: only fragmentations analogous to those shown in Scheme 3 are noted [18]. Since the structures of the two product anions arising from the competitive losses of CH_2O and MeOH through **C** are not known, we are not in a position to propose mechanisms for these processes.



C

The primary aim of this study was to investigate whether the deprotonated methyl phenyl carbonates eliminate CO_2. The answer is that loss of CO_2 is pronounced for the *ortho*-isomer but not for the other isomers (see Fig. 1). The next question is whether the mechanism proceeds through a benzyne mechanism (Scheme 2) or by way of **C** (see above and of route **A** of Scheme 1). In both cases, the *ortho*-anisyl anion, *o*-$(C_6H_4)^- - OMe$ should be the product of the reaction. It should be possible to confirm this by the measurement of the CA and CR [14,15] spectra of the source-formed product ion *m/z* 107 of Fig. 1. The CA spectrum of authentic (*o*-$C_6H_4)^- - OMe$ shows a characteristic and pronounced loss of CH_2O [20,21]: the collisional activation spectrum of *m/z* 107 (from Fig. 1 shows no loss of CH_2O). So the loss of CO_2 occurs neither by benzyne cine substitution (Scheme 2), nor through intermediate **C**.

The only other plausible mechanism for the loss of CO_2 is methyl migration through a six-centre transition state (Scheme 4), a process not possible for the analogous methyl benzoate system. The product ion formed should be the *ortho*-methylphenoxide (*ortho*-cresol) anion. The collisional activation and charge reversal spectra of isomeric cresol anions have been reported [21]. The collisional activation spectra are very weak: the only significant fragmentation (apart from loss of H·) is loss of Me·, but this loss is some fifty times less pronounced than the loss of CH_2O from *o*-$(C_6H_4)^- - OMe$ [21]. The collisional activation spectrum of the product anion *m/z* 107 ion (from Fig. 1) is weak, and loss of Me· is not detected. However any loss of Me· would certainly be lost amongst baseline noise. The CR spectra of authentic *o*-$(C_6H_4)^- - OME$ and *o*-Me-$C_6H_4O^-$ are similar except in the high mass regiion: these regions of the two spectra are shown in Fig. 2. The high mass region of the CR spectrum of source-formed *m/z* 107 anion from (*o*-$C_6H_4)^- - OCO_2Me$ is also shown for comparison in Fig. 2. The spectrum is reproducible and matches that of *o*-Me $-$ $C_6H_4O^-$. It should be noted that the CA and CR spectra of the three isomeric cresol anions are very similar [21], so we cannot use these data to differentiate between the *o*-, *m*-, and *p*-cresol anions. We conclude from available data that the product ion *m/z* 107 is not *o*-$(C_6H_4)^- - OMe$ but a cresol anion Me $-$ C_6H_4-O^-. We propose that the loss of CO_2 is initiated by methyl migration of the *ortho*-anion as shown in Scheme 4.



Scheme 4.

We have computed the reaction coordinate for the methyl migration outlined in Scheme 4 in order to test whether the proposed mechanism is plausible. These data [calculated at the B3LYP/6-311++G(*d,p*)//HF/3-21(*d*) level of theory] are summarised in Fig. 3: full geometry and energy data are listed in Table 1. These data indicate that the methyl migration is indeed a plausible mechanism. The process is stepwise with the rate determining step proceeding through six-centre transition state **E**. The barrier to the transition state is 191 kJ mol^{-1} but the initial intermediate **F** formed in this strongly exothermic process has significant excess energy and decarboxylates to form the product anion **G**. The overall process is exothermic by 276 kJ mol^{-1}. These data should be compared with those for processes **A** and **B** (Scheme 1), both of which are endothermic (+85 kJ mol^{-1}) and have barriers of 191 and 281 kJ mol^{-1} respectively. We have been unable to find any low-energy concerted pathway for the methyl migration process.

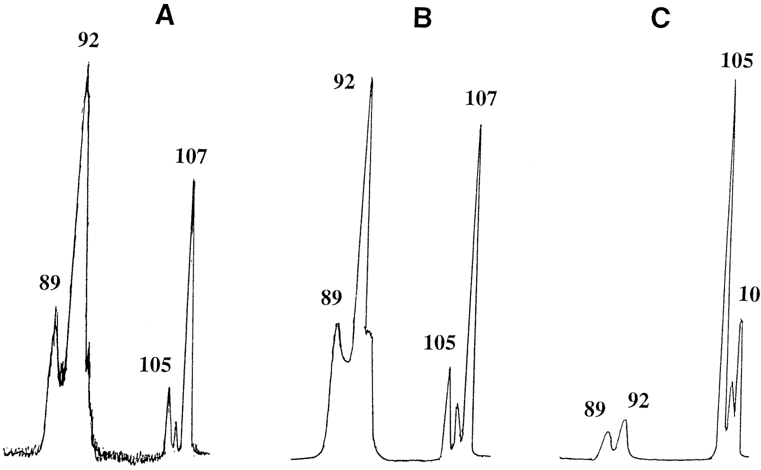


Fig. 2. High mass regions of the CR (positive ion) spectra of (**A**) *m/z* 107 from *o*-($C_6H_4^-$ − OCO_2Me, (**B**) *o*-Me − C_6H_4 − O^-, and (**C**) *o*-$(C_6H_4)^-$ − OMe. VG ZAB 2HF mass spectrometer—see sec. 2 for experimental details.

In conclusion, although *ortho*-deprotonated phenyl methyl carbonate loses carbon dioxide on collisional activation, this process does not occur by a cine-subtitution mechanism, but by the methyl migration pathway shown in detail in Fig. 3.

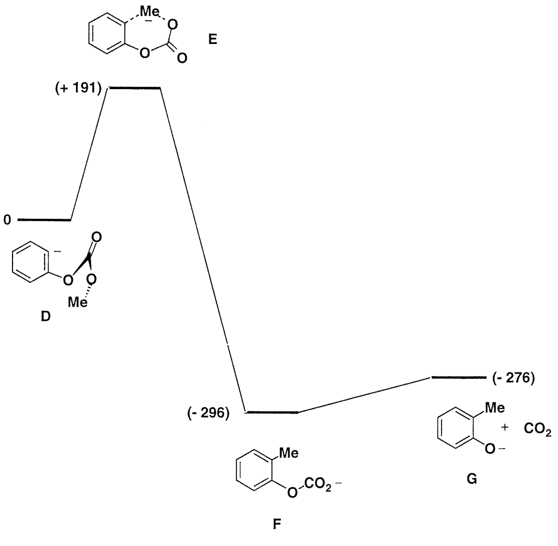
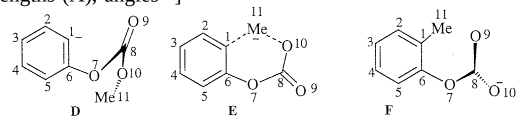


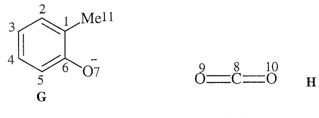
Fig. 3. Reaction coordinate for the methyl migration. B3LYP/6-311++G(*d,p*)//HF/3-21G (*d*) level of theory. For full details of geometries and energies of all species shown, see Table 1.

Table 1

Geometries and energies for species in Fig. 3 [geometries optimised at HF/3-21+G(*d*): energies—B3LYP/6-311++G(*d,p*); bond lengths (Å), angles °]



	D	E	F
Energy (Hartrees)	-534.8652320	-534.7914956	-534.9789091
Zero pt correction	0.142427	0.141464	0.143374
Relative Energy (kJ mol^{-1})	0.0	192	- 296



	G	H
Energy (Hartrees)	-346.3207155	-188.6469117
Zero point correction	0.127958	0.011619
Relative Energy of Products (kcal mol^{-1})	- 276	

	D	E	F	G	H
C_2C_1	1.4194	1.4062	1.3878	1.3781	
C_3C_2	1.3917	1.3907	1.3894	1.3875	
C_4C_3	1.3923	1.3892	1.3855	1.3909	
C_5C_4	1.3889	1.3866	1.3863	1.3809	
C_6C_5	1.3794	1.3871	1.3834	1.4327	
O_7C_6	1.4660	1.4573	1.3792	1.2996	
C_8O_7	1.3516	1.4162	1.4780		
O_9C_8	1.2089	1.2280	1.2360		1.599
$O_{10}C_8$	1.3536	1.3011	1.2468		1.599
$C_{11}O_{10}$	1.4606	1.8882			
$C_{11}C_1$		2.2650	1.5106	1.4327	
$C_3C_2C_1$	123.7	123.3	121.4	122.3	
$C_4C_3C_2$	120.2	119.6	119.5	117.7	
$C_5C_4C_3$	118.9	119.6	119.7	121.1	
$C_6C_5C_4$	117.6	119.3	120.5	122.3	
$O_7C_6C_5$	113.8	123.8	120.6	122.7	
$C_8O_7C_6$	121.6	153.0	119.1		
$O_9C_8O_7$	125.7	114.3	122.1		
$O_{10}C_8O_9$	121.5	126.6	133.1		180.0
$C_{11}C_1C_6$		90.7	119.6	117.3	
$C_{11}O_{10}C_8$	120.3	105.1			
$O_7C_6C_5C_4$	-176.8		-176.1		
$C_8C_7C_6C_5$	-139.0		-99.1		
$O_9C_8O_7C_6$	70.8		177.7		
$O_{10}C_8O_9O_7$	-173.6		-179.7		
$C_{11}C_1C_6C_5$	-154.5		179.0		

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