JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 5, 776–782 (1992)

GAS-PHASE AMBIDENT REACTIVITY OF CYCLIC ENOLATE ANIONS

IVO L. FRERIKS, LEO J. DE KONING AND NICO M. M. NIBBERING*

Institute of Mass Spectrometry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

The gas-phase reactions between cyclic enolate anions and unsaturated perfluorocarbon compounds were studied by Fourier transform ion cyclotron resonance. A correlation is observed between the experimental electron detachment threshold energies, the reaction selectivity and the ring size of the cyclic enolate anions. The results suggest that frontier orbital interactions play an important role in the course of the reactions of cyclic enolate anions, as has been shown previously for the reactions of acyclic enolate anions. In addition, the reaction selectivity of cyclic enolate anions may also be influenced by the charge distribution and by transannular interactions. In comparison with the acyclic enolate anions, the HOMO energy of the small cyclic enolate anions (C_4–C_5) has decreased and the carbanion character has increased, both of which favour reaction via carbon. The medium ring-sized cycloketone enolate anions behave very similarly to their acyclic analogues, whereas for the larger ring-sized cycloketone enolate anions (C_8–C_{12}) the reaction via the carbon nucleophilic centre gains importance as a result of the stabilization of the HOMO due to transannular interactions.

INTRODUCTION

Ambident ions can be characterized as ions in which reactive sites are connected through mesomerism.[1,2] Among ambident ions, enolate anions occupy a special position, and considerable efforts have therefore been made to understand the controlling factors in the reactions of enolate anions with alkylating agents.[1] Controlling factors which are not an intrinsic property of the enolate anion, such as solvent and counterion, are fully eliminated in the gas phase. Determination of the reaction selectivity of enolate anions in the gas phase is therefore an important way to investigate ambident reactivity as a function of the reactants.

It has been demonstrated that the reaction between an unsaturated polyfluorocarbon compound and an enolate anion in the gas phase, proceeding via either the oxygen or the carbon nucleophilic centre, yields distinctive ionic products.[3–5] This consistent reactivity pattern, together with the earlier results concerning the reactivity of both carbanions[6,7] and oxyanions,[8–10] indicate that the product ion distribution in the reaction between enolate anions and unsaturated perfluorocarbon compounds can be used as a reliable tool to probe the ambident reactivity of these anions.

The utility of a gas-phase ion–molecule reaction between an enolate anion and an unsaturated perfluorocarbon compound as a probe to investigate the intrinsic chemical properties of enolate anions in the gas phase has been shown recently in an elegant study by Brickhouse and Squires.[4]

In a previous study, we showed that the product distribution of the reaction between acyclic enolate anions of the type $R_1HC{=}CR_2O^-$ and hexafluoropropene or hexafluorobenzene in the gas phase reveals the whole range of ambident reactivity.[5] It was found that the reaction selectivity of acyclic enolate anions towards unsaturated perfluorocarbon compounds in the gas phase cannot be explained by the charge distribution in the enolate anion or the overall exothermicity of the reaction.[4,5] According to the overall exothermicity of the reaction, predominant or exclusive addition via the carbon nucleophilic centre is expected,[11] but in many reactions predominant oxygen alkylation was observed.[4,5] The charge distributions in the acetone and acetaldehyde enolate anions are identical,[12,13] but acetone enolate anion reacts with hexafluorobenzene predominantly via the carbon nucleophilic centre, whereas the acetaldehyde enolate anion reacts predominantly via the oxygen nucleophilic centre with hexafluorobenzene.[5]

There appears to be a correlation between this reaction selectivity and the experimental electron detachment threshold (and thus HOMO) energies of the acyclic enolate anions. It has also been observed that the reaction selectivity of acyclic ambident enolate

---

* Author for correspondence.

0894–3230/92/110776–07$08.50

Received 8 April 1992
Accepted 1 June 1992

anions in the gas phase depends on the unsaturated perfluorocarbon compound which acts as a substrate.[5] The nature of this correlation suggests that the reaction is controlled by specific frontier orbital interactions of the reactants rather than by the charge distribution in the enolate anion. The gas-phase reaction between acyclic enolate anions with a relatively low energetic ($< -1 \cdot 9$ eV) HOMO and unsaturated perfluorocarbon compounds proceeds preferentially via the carbon nucleophilic centre.[5] The interaction between the LUMO of the unsaturated perfluorocarbon compound and the HOMO of the enolate anion (with the largest orbital coefficient on the carbon atom) appears to be energetically most favourable. Acyclic enolate anions with a relatively high energetic ($> -1 \cdot 7$ eV) HOMO react preferentially via the oxygen nucleophilic centre. The interaction between the LUMO of the unsaturated perfluorocarbon compound and the HOMO-1 of these enolate anions (with the largest orbital coefficient on the oxygen atom) appears to be energetically most favourable.[5]

In contrast with acyclic enolate anions, not many studies have been reported on the reactivity of cyclic enolate anions in the gas phase. A pronounced ring-size influence on the reactivity was found in the gas-phase reaction of cyclic enolate anions with 6,6-dimethylfulvene[14] and hexafluoropropene.[4] Small cyclic enolate anions react mainly via the carbon nucleophilic centre, whereas the larger (C_7–C_9) cyclic enolate anions react preferentially via the oxygen end of the enolate anion. The selectivity of the reactions was related with the differences in energies gained on protonation of the enolate anion on carbon and on oxygen and hence the difference in the heats of formation of the keto and enol forms of the neutral carbonyl compounds, ΔH_{ke}. It is not possible, however, to explain the influence of the substrate on the reaction selectivity with this single-parameter model. Unfortunately, too few experimental data are available to draw any conclusion concerning the influence of the substrate on the gas-phase reactivity of cyclic enolate anions.

As mentioned above, the gas-phase ambident reactivity of acyclic enolate anions correlates with the experimentally determined electron detachment threshold energies.[5] Larger cyclic enolate anions (C_{10} and C_{12}) have electron detachment threshold energies which are almost identical with those of the small-ring (C_5) enolate anions.[15] Therefore, the chemical behaviour of these enolate anions in the gas phase is expected to be similar, based on the observed correlation between the gas-phase reactivity and the electron detachment threshold for acyclic enolate anions.

The aim of this study was to investigate systematically the influence of the substrate and ring size of the enolate anion on the reaction selectivity for a series of cyclic enolate anions.

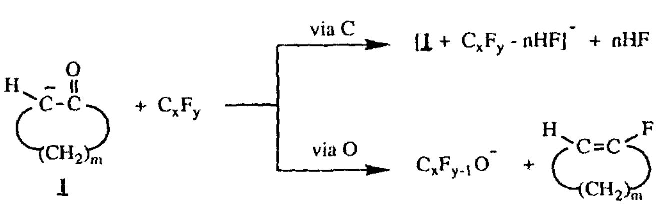
RESULTS

The primary product ion distributions have been determined for the gas-phase reactions between a series of cyclic enolate anions **1** and hexafluorobenzene, hexafluoropropene and octafluorotoluene. Following the conclusions of earlier work,[3–5] the yield of $[\mathbf{1} + C_xF_y - n\mathrm{HF}]^-$ ions represents the relative rate of the reaction via the carbon nucleophilic centre [equation (1a)], whereas the yield of $C_xF_{y-1}O^-$ ions represents the relative rate of the reaction via the oxygen nucleophilic centre [equation (1b)].

Reaction between cyclic enolate anions and hexafluoropropene

The observed reactivity of cyclic enolate anions towards hexafluoropropene under ion cyclotron resonance (ICR) conditions is analogous to earlier studied reactions of cyclic enolate anions and hexafluoropropene obtained under flowing afterglow (FA) conditions.[4] Under ICR conditions, primary product ions of the type $[\mathbf{1} + C_3F_6 - 1\mathrm{HF}]^-$ show a larger preference for an additional loss of 1–3 HF molecules than under FA conditions, where even the adduct $[\mathbf{1} + C_3F_6]^-$ is observed.[4] Collisional cooling of the intermediate reaction complexes under FA conditions results partly in thermalization of the observed reaction complexes. Under the relatively low-pressure ICR conditions this cooling does not take place, and the intermediate reaction complexes therefore have sufficient energy to overcome the activation barrier for this additional HF loss.

From the primary product ion distribution, the proportion of the reaction via carbon [equation (1a)] and oxygen [equation (1b)] have been determined. The obtained carbon alkylation percentages of **1** are given in Table 1; earlier obtained results in a flowing afterglow



(1a)

(1b)

Table 1. Percentage carbon alkylation of cyclic enolate anions in the reaction with unsaturated perfluorocarbon compounds

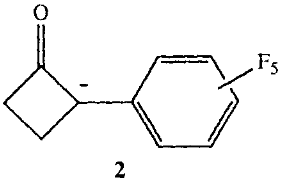
Enolate anions from	C_3F_6[a]	C_6F_6	$C_6F_5CF_3$	Electron detachment threshold[b] (eV)
cyclobutanone	100(96)	100	100	1·84 ± 0·07
cyclopentanone	100(95)	100	100	1·62 ± 0·06
cyclohexanone	87(73)	98	100	1·55 ± 0·05
cycloheptanone	2(13)	77	87	1·48 ± 0·04
cyclooctanone	9(18)	61	71	1·63 ± 0·06
cyclononanone	26(24)	65	76	1·69 ± 0·06
cyclodecanone	63	66	92	1·83 ± 0·07
cyclododecanone	68	66	93	1·90 ± 0·07

[a] Values in parentheses taken from a flowing afterglow study; see Ref. 4.
[a] Taken from Ref. 12.

apparatus, taken from the literature,[4] are included in parentheses.

Reaction between cyclic enolate anions and hexafluorobenzene

The obtained carbon alkylation percentages of **1** are summarized in Table 1. Carbon alkylation of all the studied cyclic enolate anions yielded exclusively the product ion $[\mathbf{1} + C_6F_6 - 2HF]^-$, except for carbon alkylation of the cyclobutanone enolate anion. In the reaction of the cyclobutanone enolate anion with hexafluorobenzene, 67% of the product ions are observed to be $[\mathbf{1} + C_6F_6 - 1HF]^-$. The behaviour of this reaction system can be associated with the unfavourable energetics of additional loss of HF molecules from their carbon alkylation product ion (**2**) which will result in a significant increase of the ring-strain in this product ion.



2

In the reaction of the cycloheptanone enolate anion with hexafluorobenzene, 16% of the product ions are observed to be the uncommon $C_6F_5O^- \cdot HF$ ions. This product ion is associated with reaction via the oxygen nucleophilic centre of the enolate anion.

Reaction between cyclic enolate anions and octafluorotoluene

The primary product ion distributions in the gas-phase reactions between a series of cyclic enolate anions and octafluorotoluene were determined. Carbon alkylation of all the studied cyclic enolate anions yielded exclusively the product ion $[\mathbf{1} + C_7F_8 - 2HF]^-$, except for carbon alkylation of the cyclobutanone enolate anion where, again owing to the unfavourable energetics (see above), 53% of the reaction via the carbon nucleophilic centre yielded $[\mathbf{1} + C_7F_8 - 1HF]^-$ product ions. The obtained carbon alkylation percentages of **1** are summarized in Table 1.

DISCUSSION

From the results in Table 1, it follows that cyclic enolate anions display an ambident chemical behaviour, which appears to be a function of the enolate ring size. Further, the reaction selectivity clearly depends on the nature of the substrate molecule. The cyclic enolate anions show a reaction selectivity shifted towards more carbon alkylation in the reaction with hexafluorobenzene relative to the reaction with hexafluoropropene. This is in agreement with the previously obtained reaction selectivity of acyclic enolate anions.[5] The reaction selectivity of the cyclic enolate anions is shifted even more towards carbon alkylation in the reaction with octafluorotoluene. Clearly, the ambident chemical behaviour of the cyclic enolate anions is not determined by the nature of the anions alone.

In our previous study, it was shown that the ambident chemical behaviour of acyclic enolate ions in the gas-phase reactions with hexafluoropropene and hexafluorobenzene can be rationalized with a simple MO model[5] in which specific frontier orbital interactions determine the competition between reaction via the oxygen or carbon end of the enolate anions. In this model, reaction via oxygen takes place if the orbital interaction between the HOMO-1 of the enolate anion (with the largest orbital coefficient on the more electronegative oxygen atom) and the LUMO of the unsaturated perfluorocarbon compound is energetically more favourable than the interaction between the HOMO of the enolate anion (with the largest orbital coefficient on the carbon atom) and the LUMO of the unsaturated perfluorocarbon compound. Similarly, the reaction proceeds dominantly via carbon if the orbital interaction between the HOMO of the enolate anion and the LUMO of the unsaturated perfluorocarbon compound is energetically more favourable than the interaction between the HOMO-1 of the enolate anion and the LUMO of the unsaturated perfluorocarbon compound.

With this simple model, the trend observed in this work of increasing preference for carbon alkylation in the series hexafluoropropene, hexafluorobenzene and octafluorotoluene may be rationalized in terms of the energy differences between the LUMOs of these unsaturated perfluorocarbon compounds. According to the calculated LUMO energies of hexafluoropropene (−4·53 eV) and hexafluorobenzene (−4·83 eV),[5] a larger preference for carbon alkylation of hexafluoropropene in comparison with hexafluorobenzene is to be expected. However, on formation of the encounter complex the LUMO of the unsaturated perfluocarbon compound is expected to rise in energy owing to Coulombic interactions with the enolate anion. Further, in this simple model repulsive interactions between filled orbital of the enolate anion and the unsaturated perfluorocarbon compound are not taken into account. Both repulsive and Coulombic interactions have a larger influence on the LUMO energy of the unsaturated perfluorocarbon compound than on the HOMO energy of the enolate anion. If these interactions are taken into account, the relative LUMO energies of hexafluorobenzene and hexafluoropropene may be inverted.

As mentioned above, the results in Table 1 show that the reaction selectivity is also a function of the enolate anion ring size, which may be rationalized in terms of a varying HOMO energy within the series of cyclic enolate anions.

According to Koopman's theorem, the wavelength threshold for photodetachment of an electron is a measure for the energy of the HOMO, E_{HOMO}, of the enolate anion. For the cyclic enolate anions studied, this experiment wavelength threshold, $E_{h\nu}$, has been reported[15] and the values are included in Table 1. In order to reveal the importance of HOMO–LUMO interaction, the individual HOMO energies of the enolate anions ($E_{\mathrm{HOMO}} \approx -E_{h\nu}$) have been correlated with the selectivity of the addition reactions.

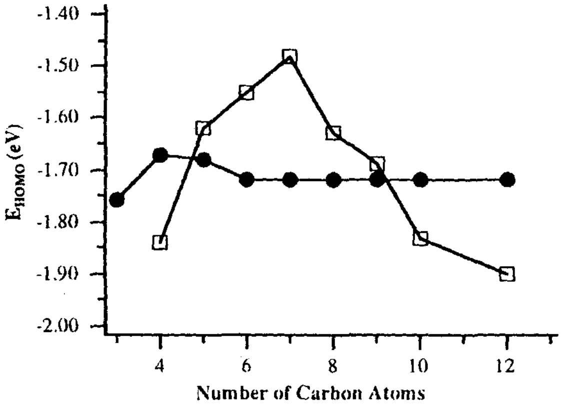


Figure 1. HOMO energies of enolate anions from (□) cyclic and (•) acyclic ketones as a function of the number of carbon atoms. Drawn lines are to guide the eyes

In Figure 1, the HOMO energies of the enolate anions from the cyclic and corresponding acyclic ketones are plotted against the number of enolate anion carbon atoms. Not all the electron detachment threshold energies of the acyclic enolate anions are known. The electron detachment threshold energies of the acyclic enolate anions of hexanone, octanone, decanone and dodecanone are taken to be identical with those of heptan-4-one. This seems justified, based on the observation that the electron detachment threshold energies of larger acyclic alkoxides are, within experimental uncertainty, independent of the alkyl chain length.[16]

In Figure 2, the selectivity of the reaction between the enolate anions from the cyclic and corresponding acyclic ketones (results for the acyclic ketones are taken from our previous study[5]) with hexafluoropropene are plotted against the number of enolate anion carbon atoms. The results show that small-sized (C_4–C_6) and large-sized (C_9–C_{12}) cyclic enolate anions preferentially react via carbon, whereas medium-sized (C_7–C_8) cyclic enolate anions react preferentially via the oxygen

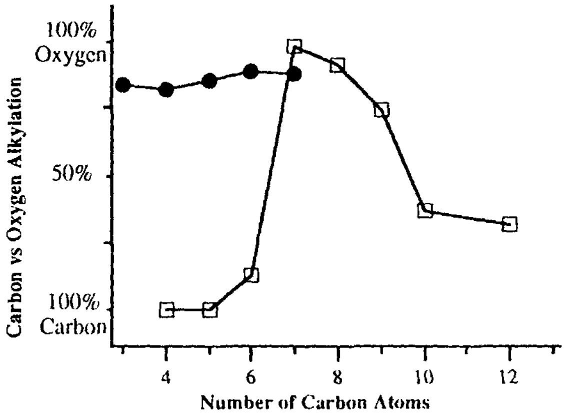


Figure 2. Selectivity of the reaction between (□) cyclic and (•) acyclic enolate anions and hexafluoropropene as a function of the number of carbon atoms. Drawn lines are to guide the eyes

nucleophilic centre. This trend has also been reported for addition reactions of cyclic enolate anions in the condensed phase.[17] The observed reactivity pattern as a function of ring size qualitatively follows the HOMO energy pattern of the cyclic enolate anions shown in Figure 1, which clearly demonstrates that specific frontier orbital interactions play a leading role in the course of the enolate anion reaction.

According to perturbation theory, stabilization of the reaction transition state depends on both the energy gap between the interacting orbitals and the local overlap of these orbitals between the interacting atoms. Because of the lack of geometrical constraints it is expected that the π-electron distribution within a series of acyclic enolate anions does not differ significantly. This implies that the energy gap between the interacting orbitals in the reactions with acyclic enolate anions is dominant. This, however, may be a false assumption for the cyclic enolate anions.

The results in Figure 1 show that the energy of the HOMO of cyclobutanone enolate anions (C_4) is about 0·2 eV lower relative to the corresponding butanone enolate anions. The energy gap between the HOMO of the enolate anion and LUMO of the unsaturated perfluorocarbon compound decreases. On the basis of this it can be expected that relative to butanone enolate anions, cyclobutanone enolate anions show a larger preference for addition via the carbon nucleophilic centre.[5] This is confirmed by the experimental results in Figure 2. The decrease in HOMO energy of the cyclobutanone enolate anion in comparison with the acyclic butanone enolate anion can be associated with an increase in the s-orbital character of the C—H bonds in the rigid cyclobutanone enolate anions as a result of which the carbon atom becomes more electronegative, which will increase the π-electron density on carbon in the enolate anion in comparison with an acyclic enolate anion, where the π-electron density is mainly localized on the oxygen atom.[12,13,18] On the other hand, conjugation with the carbonyl group in the enolate anion is expected to be hindered by the increase in ring strain in the cyclic enolate anion, which will compensate the HOMO energy gain to a certain extent. Both the increase in electronegativity of the carbon and the hindered π-conjugation result in an increase in the electron spin density on the carbon atom, giving this enolate anion a typical carbanion character, which is in agreement with the observation that this enolate anion reacts exclusively with the unsaturated perfluorocarbon compounds via carbon. Therefore, the increased preference for reaction via the carbon nucleophilic centre of the cyclobutanone enolate anion compared with the butanone enolate anion can be rationalized by both the lowering of the HOMO energy and the enhanced electron density on the carbon atom.

The HOMO energies of cyclopentanone and pentanone enolate anions (C_5) are very close (see Figure 1). For both cyclic and acyclic enolate anions the reaction channels via the oxygen and carbon nucleophilic centre are exothermic.[11] Reaction via the carbon nucleophilic centre is thermodynamically most favourable in both cases.[11] In spite of this, the ambident chemical behaviour of these corresponding enolate anions is not similar, as shown for the reactions towards hexafluoropropene in Figure 2, which show a shift from about 15% to 100% carbon alkylation on going from the pentanone to the cyclopentanone enolate anions. The different chemical behaviour of cyclic and acyclic pentanone enolate anions may be caused by different charge distributions in the enolate anions due to the ring strain in the cyclic enolate anion.

For the cyclobutanone enolate anion it was suggested (see above) that lowering of the HOMO energy is due to an increase in the electronegativity of the carbon atom, giving this enolate anion a carbanion character. The HOMO energies of cyclopentanone and pentanone enolate anions (C_5), however, are very close (see Figure 1). Apparently, the lowering of the HOMO energy due to an increase in the electronegativity of the carbon atom bearing the charge is cancelled by the destabilization due to the hindered π-conjugation with the carbonyl group in the ring-strained cyclopentanone enolate anion, as a result of which this enolate anion has more carbanion character than the corresponding enolate anion from pentanone.

For the cyclohexanone enolate anions (C_6), the HOMO energy has increased relative to the HOMO energy of the corresponding hexanone enolate anions (see Figure 1). Apparently, the energy gain due to the increase in the electronegativity of the carbon atom bearing the charge is negligible relative to the destabilization due to the hindered π-conjugation with the carbonyl group in this larger cyclic enolate anion. This hindered π-conjugation is probably responsible for the increase in the carbanion character of this cyclic enolate anion relative to the corresponding acyclic enolate anion. Therefore, in spite of the higher HOMO energy, the proportion of *C*-alkylation has increased to 87%, relative to the 14% which is associated with the enolate anion from hexanone (see Figure 2).

For the cycloheptanone enolate anion (C_7), the HOMO energy has further increased relative to the HOMO energy of the corresponding heptanone enolate anions (see Figure 1). Consequently, the proportion of *C*-alkylation has decreased to 2% relative to the 13% which is associated with the enolate anion from heptanone (see Figure 2). Evidently, the π-electron distribution in this medium ring-sized enolate anion is similar to that in the corresponding acyclic enolate anion.

For the larger cyclic enolate anions the HOMO becomes increasingly stabilized with respect to the HOMO of the corresponding acyclic enolate anions. This relative stabilization is probably due to transannular interactions. A transannular interaction is, based on the experimental data for the neutral cyclic ketones[19] and bifunctional cyclic ketones,[20–22] only to be expected for the larger (C_8–C_{12}) cyclic enolate anions. Recently, transannular interactions have been shown to influence the fragmentation process of positive ions which are formed via acetone chemical ionization of the series cycloheptene–cycloundecene.[23]

In the condensed phase, the experimentally determined content of the enol tautomer of cyclooctanone is ten times higher than that for octan-2-one and almost twenty times higher than for cycloheptanone.[19,24] This phenomenon has been explained with a transannular π-complex.[19] Spectroscopic evidence for transannular interaction in large (C_8–C_{10}) neutral bifunctional cyclic ketones has been obtained from ^{13}C and ^{17}O NMR,[20–22] x-ray crystallography[21] and photoelectron spectroscopy.[22]

A transannular interaction between the negatively charged enolate group and a hydrogen of one of the methylene groups is expected to stabilize the cyclic enolate anion more than the corresponding enolate radical, as a consequence of which the HOMO energy decreases (see Figure 1). Consequently, as expected, the proportion of *C*-alkylation increases from 2% for the cycloheptanone enolate anion (C_7) up to about 60% for the enolate anions from cyclodecanone (C_{10}) and cyclododecanone (C_{12}) (see Table 1 and Figure 2).

The observed intrinsic gas-phase reactivity of the enolate anions from cyclic ketones is also manifested in the condensed phase, where it was shown that the kinetic acidity of cyclic ketones in solution[25] follows the same order as the electron detachment thresholds and thus the HOMO energy of the cyclic enolate anions in the gas phase.[15] Small (C_4–C_5) and large (C_8–C_{12}) cyclic ketones are more acidic in solution than medium-sized cyclic ketones.

The question arises of how important frontier orbital interactions are in general for gas-phase reactions of enolate anions, e.g. in the reactions with simple alkylating reagents, such as RX. Unfortunately, very limited experimental data are available, because substitution via the carbon and oxygen nucleophilic centre of the enolate anions both results in the ionic product, X^-. In fact, only for the reaction between the enolate anion of cyclohexanone and CH_3Br has it been established from the analysis of the neutral products that exclusive *O*-alkylation occurs in the gas phase.[26] This is in contrast with the reactions towards perfluorocarbon compounds in which the enolate anion from cyclohexanone strongly favours addition via carbon.[4]

It may be evident that the energy gained in these specific frontier orbital interactions can only compete with the energy gained in the assumed strongly electrostatic interactions if the energy gap between the frontier orbital of the two reactants is small. Moreover, the overlap of the HOMO of the enolate anion and the LUMO of the substrate is an important parameter.

For the reactions between the enolate anions and unsaturated perfluorocarbon compounds both the HOMO of the enolate anions and the LUMO of the unsaturated perfluorocarbon compounds are of the π type, which allows a favourable overlap, eventually resulting in the formation of a σ complex. For the reactions between the enolate anions and RX, the π-type HOMO has to overlap with the σ^*-type LUMO of RX, which may be less favourable, and which synchronously results in R—X bond cleavage. Therefore, even if the energy of the HOMO and LUMO are close, it is difficult to predict if the frontier orbital interactions are still stronger than the electrostatic interactions.

The LUMO energy of CH_3Br is not known but for this discussion can roughly be estimated by $E_{(n\rightarrow\sigma^*)} - E_{\text{ionization}} = 6{\cdot}1$ (204 nm)[27] $- 10{\cdot}5$[16] $\approx -4{\cdot}4$ eV, which is surprisingly close to the calculated LUMO energy of hexafluoropropene of $-4{\cdot}53$ eV.[5] Hence it may be expected that the reaction with CH_3Br would show similar ambident behaviour to the reaction with hexafluoropropene, which is in contrast with the experimental findings. Evidently, owing to the poor frontier orbital overlap in the reaction with CH_3Br, the electrostatic interactions are dominant and favour reaction via oxygen.

CONCLUSIONS

Cyclic enolate anions exhibit an ambident chemical behaviour in their reactions with hexafluoropropene, hexafluorobenzene and octafluorotoluene. It appears that frontier orbital interactions play an important role in the course of the reactions of both acyclic and cyclic enolate anions. The reaction selectivity of cyclic enolate anions also may be influenced by the charge distributions and transannular interactions in the cyclic enolate anions. In comparison with the acyclic enolate anions, the HOMO energy of the small cyclic enolate anions (C_4–C_5) has decreased and the carbanion character has increased, both of which favours reaction via carbon. The medium ring-sized cycloketone enolate anions behave very similarly to their acyclic analogues, whereas for the larger ring-sized cycloketone enolate anions (C_8–C_{12}) the reaction via the carbon nucleophilic centre gains importance as a result of the stabilization of the HOMO due to transannular interaction.

EXPERIMENTAL

Experiments were carrried with a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer built at the University of Amsterdam and equipped with a Bruker 1·4 T electromagnet and a 1 × 1 × 1 in cell. Details of the instrument and general operating and experimental procedures have been described previously.[28] Enolate anions were generated via proton abstraction from the corresponding cyclic ketones using primarily generated amide as the base.

The total pressure was kept typically at *ca* 8×10^{-5} Pa. The temperature of the FT-ICR cell was *ca* 330 K as measured by a thermocouple on the trapping plate opposite to the filament. The segmented Fourier transform (SEFT) procedure,[29] developed in our laboratory, was used to determine relative ion abundances with an accuracy of better than 1%.

Materials. All chemicals employed were commercially available and were used without further purification. They were purchased from Aldrich (Brussels, Belgium), except for ammonia (Hoek Loos, Schiedam, The Netherlands) and cyclopentanone (Merck, Amsterdam, The Netherlands).

ACKNOWLEDGEMENT

Financial support from the Netherlands Organization for Scientific Research (SON/NWO) is gratefully acknowledged.

REFERENCES

1. O. A. Reutov, I. P. Beletskaya and A. L. Kurts, in *Ambident Anions*, edited by J. P. Michael, pp. 1–146. Consultants Bureau, New York (1983).
2. N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *J. Am. Chem. Soc.* **77**, 6269–6280 (1955).
3. S. Ingemann, N. M. M. Nibbering, S. A. Sullivan and C. H. DePuy *J. Am. Chem. Soc.* **104**, 6520–6527 (1982).
4. M. D. Brickhouse and R. R. Squires, *J. Phys. Org. Chem.* **2**, 389–409 (1989).
5. I. L. Freriks, L. J. de Koning and N. M. M. Nibbering, *J. Am. Chem. Soc.* **113**, 9119–9124 (1991).
6. J. H. J. Dawson and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Phys.* **33**, 3–19 (1980).
7. J. C Kleingeld and N. M. M. Nibbering, *Recl. Trav. Chim. Pays-Bas* **103**, 87–90 (1984).
8. S. M. J. Briscese and J. M. Riveros, *J. Am. Chem. Soc.* **97**, 230–231 (1975).
9. J. M. Riveros and K. Takashima, *Can. J. Chem.* **54**, 1839–1840 (1976).
10. S. A. Sullivan and J. L. Beauchamp, *J. Am. Chem. Soc.* **99**, 5017–5022 (1977).
11. Calculated from S. W. Benson, *Thermochemical Kinetics*, 2nd ed. Wiley–Interscience, New York (1976).
12. K. B. Wiberg, C. M. Breneman and T. J. LePage, *J. Am. Chem. Soc.* **112**, 61–72 (1990).
13. K. B. Wiberg, *J. Am. Chem. Soc.* **112**, 4177–4182 (1990).
14. M. D. Brickhouse and R. R. Squires *J. Am. Chem. Soc.* **110**, 2706–2714 (1988).
15. A. H. Zimmerman, R. L. Jackson, B. K. Janousek and J. I. Brauman, *J. Am. Chem. Soc.* **100**, 4674–4676 (1978).
16. S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin and W. G. Mallard, *Gas-Phase Ion and Neutral Thermochemistry*; *J. Phys. Chem. Ref. Data* **17**, Suppl. 1 (1988).
17. G. J. Heiszwolf and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas* **89**, 1153–1169 (1970).
18. I. Fleming, *Frontier Orbitals and Organic Reactions*, Wiley–Interscience, New York (1976). pp. 22–32, 43–45.
19. A. Gero, *J. Org. Chem.* **26**, 3156–3157 (1961).
20. T. T. Nakashima and G. E. Maciel, *Org. Magn. Reson.* **4**, 321–326 (1972).
21. G. Spanka, R. Boese and P. Rademacher, *J. Org. Chem.* **52**, 3362–3367 (1987).
22. G. Spanka, P. Rademacher and H. Duddeck, *J. Chem. Soc., Perkin Trans. 2* 2119–2121 (1989).
23. M. Vairamani, M. S. Rajeev and K. V. Kumar, *Rapid Commun. Mass Spectrom.* **5**, 35–36 (1991).
24. A. Gero, *J. Org. Chem.* **19**, 1960–1970 (1954).
25. A. Schriesheim, R. J. Muller and C. A. Rowe, Jr, *J. Am. Chem. Soc.* **84**, 3164–3168 (1962).
26. M. E. Jones, S. R. Kass, J. Filley, R. M. Barkley and G. B. Ellison, *J. Am. Chem. Soc.* **107**, 109–115 (1985).
27. M. Hesse, H. Meier and B. Zeeh, *Spektroskopische Methoden in der Organischen Chemie*, 2nd ed., p. 13. Thieme Verlag, Stuttgart (1984).
28. L. J. de Koning and N. M. M. Nibbering, *J. Am. Chem. Soc.* **109**, 1715–1722 (1987), and references cited therein.
29. L. J. de Koning, C. W. F. Kort, F. A. Pinkse and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Processes* **95**, 71–92 (1989).