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Homoconjugation vs. Charge Dipole Interaction Effects in the Stabilization of Carbanions in the Gas Phase

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Abstract: This paper reports the observation of a class of stable gas-phase *primary* carbanions in which stability is conferred either by an intramolecular charge dipole interaction or by homoconjugative effects. The relative contribution from these two stabilizing influences is discussed for the ions $^-CH_2C(CH_3)_2CHO$ and $^-CH_2C(CH_3)_2NO$, and it is shown that the charge dipole interaction predominates. In the limit such anions could ring close, but it is shown that the anion derived by proton abstraction from a labeled cyclopropanol ring opens and rearranges by a specific bimolecular process.

Introduction

The concept of homoconjugation in anions[1] and its application in the generation of synthetically useful species such as homoenolate anions[2] in the liquid phase has received considerable attention. However, as far as we are aware, no explicit reports of the generation or reactions of homoconjugative anions in the gas phase have appeared. In fact, the trends in gas-phase acidities which have been measured for a large number of compounds[3] can all be explained without invoking factors other than polarizability charge delocalizing π resonance, and inductive or hyperconjugative effects.

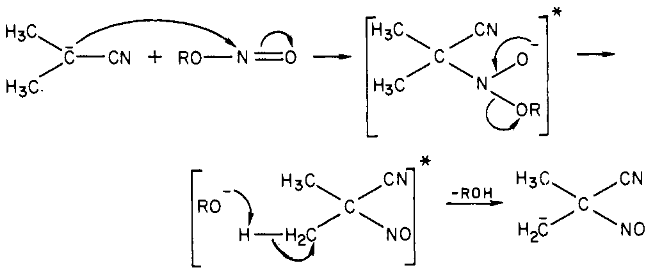
We now wish to report some results from an ion cyclotron resonance[4] (ICR) study into the generation of some carbanions which would seem to possess all the prerequisites for exhibiting homoconjugative effects. The present work owes its inception to the observation of reaction 1 during our earlier study of ion–molecule reactions of some aliphatic nitrites:[5]

$$\underset{m/z\ 68}{(CH_3)_2\bar{C}CN} + RONO \rightarrow \underset{m/z\ 97}{C_4H_5N_2O^-} + ROH \qquad (1)$$

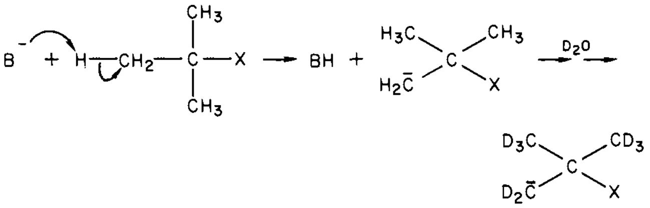
The mechanism of this reaction is not known, but it probably proceeds by the complex ion mechanism advanced by Stewart et al.[6] for gas-phase ion–molecule reactions (Scheme I). In the absence of interactions between the primary carbanionic site and the polar groups in the proposed product ion structure, this reaction is estimated to be highly endothermic (~40 kcal mol^{-1} when CH_3ONO is the substrate[7]).

There does not seem to be any more satisfactory structure for the m/z 97 ion. It appears therefore that the proposed structure must be correct and that there must therefore be considerable stabilization of the charge by the polar CN and NO groups. This stabilization may be due to various interactions such as through-bond and charge dipole interactions, perhaps hyperconjugation of the CN and NO groups or a homoconjugative interaction of their π system with the carbanionic site. A more specific investigation of ions of the type generated in reaction 1 is called for, and 2-methyl-2-nitrosopropane (t-BuNO) has been selected for a more detailed study.

Scheme I



Scheme II



$B^- = OH^-, OD^-, NH_2^-$
X = NO, CHO

Experimental Section

ICR mass spectra were recorded on a much modified Varian V5903 instrument. Pumping was by a 2-in. oil diffusion pump, and sample pressures were measured only approximately on an uncalibrated ionization gauge placed in a side arm of the main pumping line near the diffusion pump. Spectra were recorded using a home-made flat four-section drift cell (cross section 26 × 12 mm) as described in ref 8 which also outlines typical operating conditions. The reactant ions NH_2^-, OH^-, and RO^- were generated from NH_3 (5 eV), H_2O (5.8 eV, via H^-), and RONO (nonresonant process). All reactions described were consistent with the results of double resonance experiments.

2,2-Dimethylpropionaldehyde and 2,2-dimethylpropionitrile were Aldrich samples. 1,1-Dimethyl-1-nitroethane,[9] 2-methyl-2-nitrosopropane,[10] and 2,2-dideuterio-1-hydroxy-1-methoxycyclopropane[11] had

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[1] A. Nickon, J. L. Lambert, J. E. Oliver, D. F. Covey, and J. Morgan, *J. Am. Chem. Soc.*, **98**, 2593 (1976).

[2] (a) D. E. Evans, J. M. Takacs, and K. M. Hurst, *J. Am. Chem. Soc.*, **101**, 371 (1979), and references therein; (b) E. Nakamura and I. Kuwajima, *ibid.*, **99**, 7360 (1977), and references therein; (c) J. C. Stowell, "Carbanions in Organic Synthesis", Wiley, New York, 1979.

[3] (a) J. E. Bartmess, J. A. Scott, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **101**, 6046, 6056 (1979); (b) J. E. Bartmess and R. T. McIver, Jr., "Gas Phase Ion Chemistry", Vol. 2, M. T. Bowers, Ed., Academic Press, New York, 1979, Chapter 11.

[4] T. A. Lehman and M. M. Bursey, "Ion Cyclotron Resonance Spectrometry", Wiley-Interscience, New York, 1976.

[5] A. J. Noest and N. M. M. Nibbering, *Adv. Mass Spectrom.*, in press.

[6] J. H. Stewart, R. H. Shapiro, C. H. DePuy, and V. M. Bierbaum, *J. Am. Chem. Soc.*, **99**, 7650 (1977).

[7] The heat of formation of $(CH_3)_2CCN^-$ has been taken from ref 3a. The heats of formation of CH_3ONO and CH_3OH have been taken from ref 14b. The heat of formation of 2-cyano-2-nitrosopropane has been calculated by use of the group equivalent values given in ref 14b and that of the NO group given in ref 14c. The heat of formation of the $(M - H)^-$ ion of 2-cyano-2-nitrosopropane has then been estimated by taking the gas-phase acidity of methane from ref 3a as an approximation for the acidity of this compound.

[8] J. H. J. Dawson, A. J. Noest, and N. M. M. Nibbering, *Int. J. Mass Spectrom. Ion Phys.*, **29**, 205 (1979).

[9] N. Kornblum, R. J. Clutter, and W. J. Jones, *J. Am. Chem. Soc.*, **78**, 4003 (1956).

[10] J. A. Maassen and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **90**, 373 (1971).

[11] M. W. E. M. van Tilborg, R. van Doorn, and N. M. M. Nibbering, *J. Am. Chem. Soc.*, **101**, 7617 (1979).

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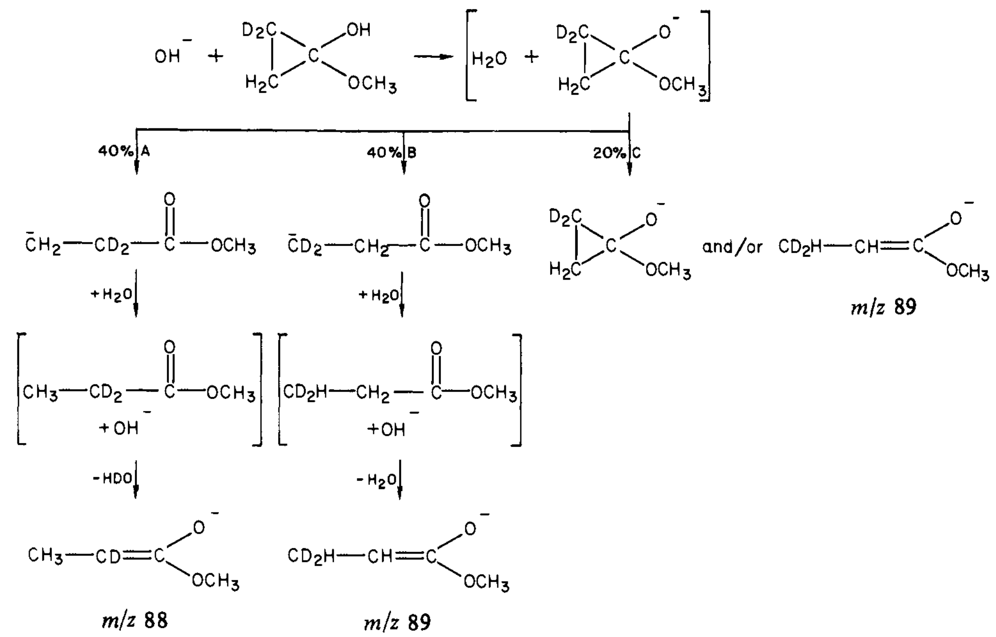
Scheme III



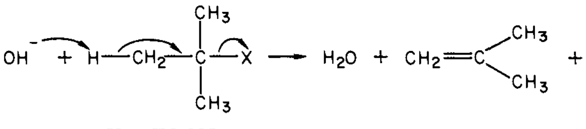
been previously synthesized in our laboratory.

Results and Discussion

Hydrogen–Deuterium Exchange Phenomena. Both hydroxide and amide anions abstract a proton from *t*-BuNO with unexpected ease to give $(M - H)^-$ ions which are stable with respect to electron detachment under our experimental conditions (observation time several milliseconds, pressure 10^{-6} to 10^{-5} torr). Bracketing experiments show that the gas-phase acidity $\Delta H°_{acid}$ of *t*-BuNO lies between that of water[3] (391 kcal mol^{-1}) and methanol[3] (379 kcal mol^{-1}). Significantly, hydrogen/deuterium exchange is observed when the $(M - H)^-$ ions are formed in the presence of D_2O. Increasing the partial pressure of D_2O from 10^{-6} to 5×10^{-5} torr eventually results in the incorporation of up to eight deuterium atoms into some of the $(M - H)^-$ ions. Such hydrogen/deuterium exchange processes have been used as a valuable probe into gas-phase ion structures.[12] The results obtained here are consistent with the view that no skeletal rearrangements have occurred in the $C_3H_8CNO^-$ ions.

A similar behavior is found for the related compound 2,2-dimethylpropionaldehyde (*t*-BuCHO). Its gas-phase acidity is also found to lie between that of water[3] and methanol,[3] and with D_2O eight hydrogen atoms in the $C_5H_9O^-$ ions can be exchanged. The single nonexchangeable hydrogen atom must be the original aldehydic hydrogen atom. These observations concerning *t*-BuNO and *t*-BuCHO are summarized in Scheme II.

Two related compounds, *t*-BuCN and *t*-BuNO$_2$, have been tested for analogous behavior, but it has not yet been found possible to form stable $(M - H)^-$ ions from them. Instead, reaction with strong bases such as OH^- and NH_2^- only leads to the formation of CN^- and NO_2^-, respectively. These ions are most probably formed via an E2 elimination process[13] as shown in reaction 2.



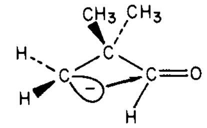
$$OH^- + H{-}CH_2{-}C(CH_3)_2{-}X \rightarrow H_2O + CH_2{=}C(CH_3)_2 + X^- \quad (2)$$

$X = CN, NO_2$

The exothermicity of reaction 2 is calculated to be 14 kcal mol^{-1} for X = CN and 54 kcal mol^{-1} for $X = NO_2$.[14] Presumably reaction 2 does not occur when X = NO or CHO, because they are not such good leaving groups. The heat of reaction 2 is calculated to be 0 kcal mol^{-1} for X = NO and 39–48 kcal mol^{-1} endothermic for X = CHO.[14]

Acidities

It is now necessary to explain the unexpectedly high acidities observed for *t*-BuNO and *t*-BuCHO. Taking the gas-phase acidity of methane[3] ($\Delta H°_{acid} = 416$ kcal mol^{-1}) as an approximation for the *tert*-butyl protons in the absence of stabilizing factors operating in the anions, one must conclude that the $(M - H)^-$ ions of *t*-BuNO and *t*-BuCHO are stabilized by 25–37 kcal mol^{-1} (vide supra). It is our opinion that a large part of this stabilization energy will be due to a simple interaction between the charge in an sp^3 orbital and the dipole moment of the functional group as indicated for the $(M - H)^-$ ions of *t*-BuCHO:



Taking the formula $E = -q\mu \cos \vartheta / r^2$ and favorable conformations, it is roughly estimated that 19 and 21 kcal mol^{-1} stabilization energy will be available to the $(M - H)^-$ ions of *t*-BuNO and *t*-BuCHO, respectively.[15] Some further stabilization energy may come from polarizability effects and from hyperconjugative contributions from the polar groups, but this is difficult to quantify. There remains the question of whether or not homoconjugative effects also contribute to the stabilization of these anions. Re-

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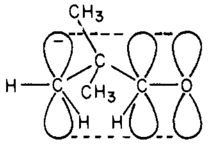
(12) (a) C. H. DePuy, V. M. Bierbaum, G. K. King, and R. H. Shapiro, *J. Am. Chem. Soc.*, **100**, 2921 (1978); (b) J. H. Dawson, Th. A. M. Kaandorp, and N. M. M. Nibbering, *Org. Mass Spectrom.*, **12**, 330 (1977).

(13) (a) D. P. Ridge and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 637, 3595 (1974); (b) S. A. Sullivan and J. L. Beauchamp, *ibid.*, **98**, 1160 (1976).

(14) (a) The heats of formation of H_2O, $(CH_3)_2C{=}CH_2$, OH^-, CN^-, NO_2^-, and NO^- have been taken from H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data*, **6**, Suppl. 1 (1977). (b) The heats of formation of $(CH_3)_3CCHO$, $(CH_3)_3CNO_2$, and $(CH_3)_3CCN$ have been calculated by use of the table of group equivalent values given by J. L. Franklin, J. F. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Ions", NSRDS-NBS 26, National Bureau of Standards, Washington, D.C., 1969. (c) The heat of formation of $(CH_3)_3CNO$ has been taken from S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969). (d) The heat of formation of HCO^- is from Z. Karpas and F. S. Klein, *Int. J. Mass Spectrom. Ion Phys.*, **18**, 65 (1975).

(15) μ(-NO) = 2.5 D has been taken from D. L. Hammick et al., *J. Chem. Soc.*, 742 (1932), and μ(-CHO) = 2.69D has been taken from R. D. Nelson, Jr., D. R. Lide, Jr., and A. A. Maryott, "Selected Values of Electric Dipole Moments for Molecules in the Gas Phase", NSRDS-NBS 10, National Bureau of Standards, Washington, D. C., 1967. Geometry values used for *t*-BuNO and *t*-BuCHO are r = 2.9-3 Å and $\vartheta \leq 20°$.

hybridization of the charge bearing sp^3 orbital to a p orbital is then required to allow a bonding overlap with the π system of the polar groups as indicated for the $(M - H)^-$ ions of *t*-BuCHO:



In theory such a homoconjugation could eventually lead to ring closure and isomerization of the ion into a cyclopropoxide anion. However, the H/D exchange experiments mentioned previously indicate that if such an isomerization occurs at all, it must be very slow. In order to investigate whether such a ring closure is energetically accessible, we have studied the behavior of the ring-closed ion generated by proton abstraction from 2,2-dideuterio-1-hydroxy-1-methoxycyclopropane.[11] Interaction with OH^-/H_2O ($P_{H_2O} = 3 \times 10^{-6}$ torr) yields two major product ions at m/z 88 and 89 with relative intensities of 40 and 60%, respectively. Their formation in this ratio is rationalized in Scheme III. If secondary isotope effects are neglected, it may be deduced that at most 20% of the ions remain ring-closed and/or have suffered from an internal 1,2-proton shift after ring opening.

It might have been anticipated that a highly exothermic proton shift from the C_2 to the C_3 position would occur immediately after ring opening, but if this were the case no m/z 88 signal would have been observed. This result thus confirms the theoretical expectation that 1,2-H shifts will be disallowed in anions.

The results show that most of the cyclopropoxide anions are ring opened, reprotonated, and immediately deprotonated at a different site to yield the more stable isomeric enol ions. This gas-phase process closely parallels the results obtained earlier in the liquid-phase chemistry of some cyclopropanol systems.[16] Reaction of 2,2-dideuterio-1-hydroxy-1-methoxycyclopropane with OD^-/D_2O at $P_{D_2O} = 3 \times 10^{-6}$ torr gives 16% m/z 88 (d_1), 63% m/z 89 (d_2), and 21% m/z 90 (d_3) ions. This observation provides evidence that the reprotonation step of the ring-opened ions involves mostly the *same* HDO molecule which is formed in the initial proton abstraction step; according to Scheme III 20% m/z 88, 60% m/z 89, and 20% m/z 90 ions are then expected to be generated. At higher pressures of H_2O, path C in Scheme III becomes less significant (10% at $P_{H_2O} = 3 \times 10^{-5}$ torr). This leads to the prediction that the results of the OD^-/D_2O experiment at this pressure should be 22.5% m/z 88, 55% m/z 89, and 22.5% m/z 90, whereas the observed percentages are 20, 50, and 30, respectively. The discrepancy here could well be due to an exchange of the HDO molecule in the initial reaction complex with a D_2O molecule from the bath gas.

These results lead us to the conclusion that no significant activation energy barrier exists between the cyclopropoxide anion and its opened isomer; the latter is a distinctly lower energy structure. This substantiates the view that the $(M - H)^-$ ions of *t*-BuNO and *t*-BuCHO retain the structures with which they were formed and that any homoconjugation which may occur does not lead to the formation of permanently ring-closed ions. Further studies on the 2,2-dimethylcyclopropoxide anion and on various other small ring compound derived anions[17] are in progress and will be reported in subsequent papers.

Acknowledgment. The authors wish to thank the Netherlands Organization for Pure Research (SON/ZWO) for the purchase of the basic ion cyclotron resonance mass spectrometer. They also wish to thank Dr. J. H. J. Dawson for valuable discussions and critical comments.

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(16) D. H. Gibson and C. H. DePuy, *Chem. Rev.*, **74**, 605 (1974).

(17) For example, we have found recently that NH_2^- and OH^- react with cyclopropylamine not only to generate $(M - 1)^-$ ions, but also to form abundant $(M - 3)^-$ ions. The latter are thought to be due to loss of molecular hydrogen from the $(M - H)^-$ ions, a process which is facilitated by the highly exothermic opening of the cyclopropyl ring. This is similar to the established behavior of propylene oxide, reported by V. M. Bierbaum, C. H. DePuy, R. H. Shapiro, and J. W. Stewart, *J. Am. Chem. Soc.*, **98**, 4229 (1976).