Theoretical Studies on Gas-Phase Reactions of Negative Ions with Alkyl Nitrites

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Received April 28, 2000

Gas-Phase reactions of methyl and ethyl nitrites with anionic nucleophiles of SH^-, F^- and OH^- are investigated theoretically at the MP2/6-311+G* level. The S_N2 processes are all highly exothermic and proceed with a typical double-well reaction coordinate profile. The elimination reactions of methyl nitrite with SH^- and F^- are double-well energy surface processes, with stabilized product complexes of $NO^-\cdots H_2S$ and $NO^-\cdots HF$, proceeding by an E1cb-like E2 mechanism. The β-elimination of ethyl nitrite is an E2 type process. The α-elimination reactions of methyl and ethyl nitrites with OH^- have triple-well energy profiles of E1cb pathway with an α-carbanion intermediate which is stabilized by the vicinal $n_{C\alpha}$-$\sigma^*_{O\text{-}N}$ charge transfer interactions. Complexation of methyl carbanion with HF seems to provide a stable intermediate within a triple-well energy profile of E1cb channel in the reaction of F^- with methyl nitrite.

Introduction

Alkyl nitrites are known to undergo many different types of reactions in the gas phase as well as in solution.[1] In solution, nitrosation of amines takes place by alkyl nitrites concertedly in aqueous media but is changed to a stepwise mechanism in nonaqueous solvents.[2] Carbanions react readily with alkyl nitrites to form nitroso compounds and to oximes by tautomerization.[3] The nitrite ion is also a good leaving group in substitution and elimination reactions.[3] In the gas phase, alkyl nitrites are used as sources of alkoxide ions.[4] Due to this diversity of reaction pathways, alkyl nitrites have been used as useful substrates for gas-phase synthesis reactions and for mechanistic studies of gas-phase ion-molecule interactions.[1, 3, 4]

Negative ion reactions of a variety of alkyl nitrites have been studied using an ion cyclotron resonance (ICR) spectrometer.[4] DePuy and coworkers have reported a flowing afterglow (FA) and selected ion flow tube (SIFT) studies of the reactions of alkyl nitrites with a variety of negative ions.[3] The reactions of fluoride ion have been shown to proceed by substitution and/or by elimination channels. Although they have also used NH_2^- and OH^- ions, detailed analysis of the alkyl nitrites reactions with these anions were not given.

In this work, we examined theoretically the gas-phase reactions of anions, SH^-, F^- and OH^-, with methyl and ethyl nitrites in some detail. The purpose of this study is to determine the influence of base strength of the anion necleophiles and alkyl groups of nitrites on the reaction mechanisms and product distributions. Wherever possible, we have compared our results with the experiment, and quantitative analyses are presented for the potential energy profiles of the reactions which were experimentally inaccessible.

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Calculations

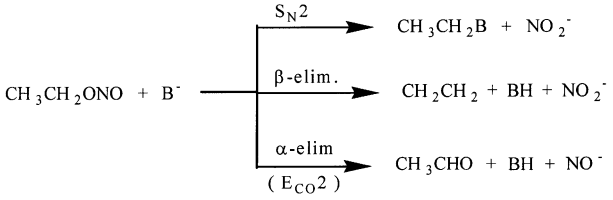
All calculations were performed with the program Gaussian 98.[5] Energetics are reported at the MP2 level using the 6-311+G* basis sets. All the stationary point structures were fully optimized and characterized by vibrational frequency calculations. The zero-point energies and the thermal energy corrections from 0 to 298 K were obtained from calculations of vibrational frequencies at the RHF level. The entropy terms ($-T\Delta S$) were added to arrive at the free energy changes (ΔG). The natural bond orbital (NBO) analyses [6] were carried out to determine proximate (n-σ^*, σ-σ^* etc.) delocalization interaction energies.[6,7] Calculations of proton affinities were carried out at the G2(+)(MP2) level.[8]

Results and Discussion

The nitrite ion is a potentially good leaving group in substitution (S_N2) and in β-elimination reactions. In addition, eliminations involving α-proton abstraction by a base, B^-, are also possible leading to a carbon-oxygen double bond formation ($E_{CO}2$ process in Scheme 1).[3] For methyl nitrite, β-elimination with an expulsion of nitrite ion is not possible and only the S_N2 and a-elimination ($E_{CO}2$) processes are found to occur in the gas phase experimentally.[3]

Proton-transfer Energies (PTE).

The elimination reactions are induced by abstraction of an α- or β-proton of the alkyl group by a base (B^-) so that proton-transfer from the alkyl group to B^- is critical in deter-



Scheme 1

mining the reactivity of elimination processes. We have therefore examined proton affinities (PA) of the anionic bases (ΔH^o for $BH \rightarrow B^- + H^+$), and α- and β-carbanions of the alkyl nitrites (ΔH^o for $\equiv CH \rightarrow \equiv C^- + H^+$). The proton-transfer energies (PTE $\equiv \delta\Delta H^o$) from an alkyl nitrite to a base (eq. 1) can be given by eq. 2 using the two proton affinities.

$$\equiv CH + B^- \rightarrow \equiv C^- + BH \quad (1)$$

$$\delta\Delta H^o = PA\,(C^-) - PA\,(B^-) \quad (2)$$

The PAs and PTEs are summarized in Table 1.

We note that β-proton transfers to anionic bases $B^- = F^-$ and OH^- are exothermic, whereas α-proton transfers are exothermic only with a strong base OH^-. The abstraction of an α-proton from methyl nitrite requires more energy (by *ca.* 6 kcal mol^{-1}) than that from ethyl nitrite. These trends suggest that β-elimination is much more facile than α-elimination and α-elimination of methyl nitrite should be significantly more difficult than that of ethyl nitrite.

S_N2 Reactions: Energetics and extents of bond-formation and -cleavage in the transition state (TS) as defined by percentage bond-order changes in the TS, $\%\Delta n^{\neq}$ in eq. 3,[9] for r_1(C_α-B bond) and r_2(C_α-LG bond) are summarized in Table 2.

$$\%\Delta n^{\neq} = \frac{\exp(-r^{\neq}/a) - \exp(-r_R/a)}{\exp(-r_P/a) - \exp(-r_R/a)} \times 100 \quad (3)$$

In eq. 3, $r^{\neq}$, r_P and r_R are bond lengths in the TS, product and reactant respectively, and a was fixed to 0.7. All the S_N2 processes had double-well potential energy surface (PES), Figure 1. The TS is below reactants level ($\Delta G^{\neq} < 0$) only for the reactions of strongest anionic base, OH^-, although all the S_N2 processes are highly exothermic ($\Delta G^o \ll 0$).

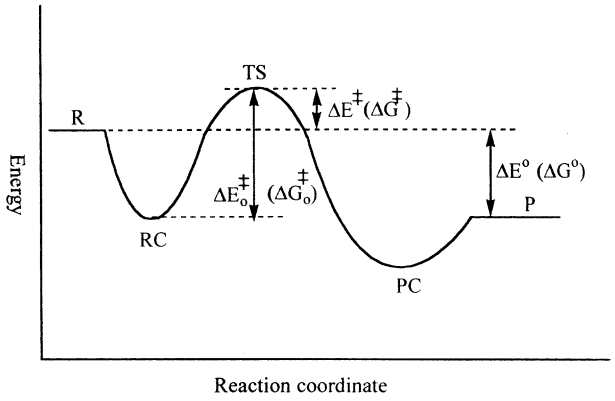


Figure 1. Double-well potential energy surface.

Representative MP2/6-311+G* structures of reactant complex, TS, and product complex are given in Figure 2.

The activation free energy ($\Delta G^{\neq}$) decreases with exothermicity ($-\Delta G^o$) and hence the S_N2 reactivity is in general determined by the thermodynamic driving force. The gas-phase S_N2 reactions with the weakest base, SH^-, have the highest barriers ($\Delta G^{\neq} \cong 11$~15 kcal mol^{-1}). This may be ascribed partly to a greater degree of leaving group (NO_2^-)

Table 1. Proton-transfer energies [PTE: $\delta\Delta H^o$=PA(C^-) PA(B^-), kcal mol^{-1}] of α-(C_α) and β-(C_β) proton of alkyl nitrites to bases (SH^-, F^- and OH^-)

	CH_3CH_2ONO		CH_3ONO	ΔPTE
	$^-C_\beta$	$^-C_\alpha$		
SH^-	116	37.6	43.6	0.0
F^-	-18.0	18.0	24.0	-19.6
OH^-	-36.3	-0.3	5.7	-37.9
ΔPTE	0.0	36.0	42.0	

PAs are (G2(+)(MP2)), [experimental] [(a)]: (350.9) [351.4], (370.5) [371.3] and (388.8) [390.5] for SH^-, F^- and OH^-, respectively, and (352.5), (388.5), and (394.5) for β-carbanion ($^-C_\beta$) and α-carbanion ($^-C_\alpha$) of ethyl nitrite and α-carbanion ($^-C_\alpha$) of methyl nitrite, respectively, in kcal mol^{-1}. [(a)]Gronert, S. *J. Am. Chem. Soc.* **1993**, *115*, 10258.

Table 2. Energetics (kcal mol^{-1}) and extents ($\%\Delta n^{\neq}$) of bond-formation (r_1) and cleavage (r_2) for S_N2 processes

	CH_3ONO			CH_3CH_2ONO		
B^-	SH^-	F^-	OH^-	SH^-	F^-	OH^-
$\Delta G^{\neq}$ [a]	11.4	1.1	-2.1	15.4	3.6	-1.0
ΔG^o [b]	-19.1	-22.8	-45.0	-18.1	-24.4	-75.9
$\Delta G^{\neq}_o$ [c]	16.3	12.5	10.3	21.0	15.2	11.3
$\%\Delta n^{\neq}$ (r_1)	40	46	38	38	45	37
$\%\Delta n^{\neq}$ (r_2)	48	42	37	50	45	15

[a]Activation free energy from the separated reactants. [b]Free energy of reaction. [c]Central barrier : barrier height relative to the reactant complex.

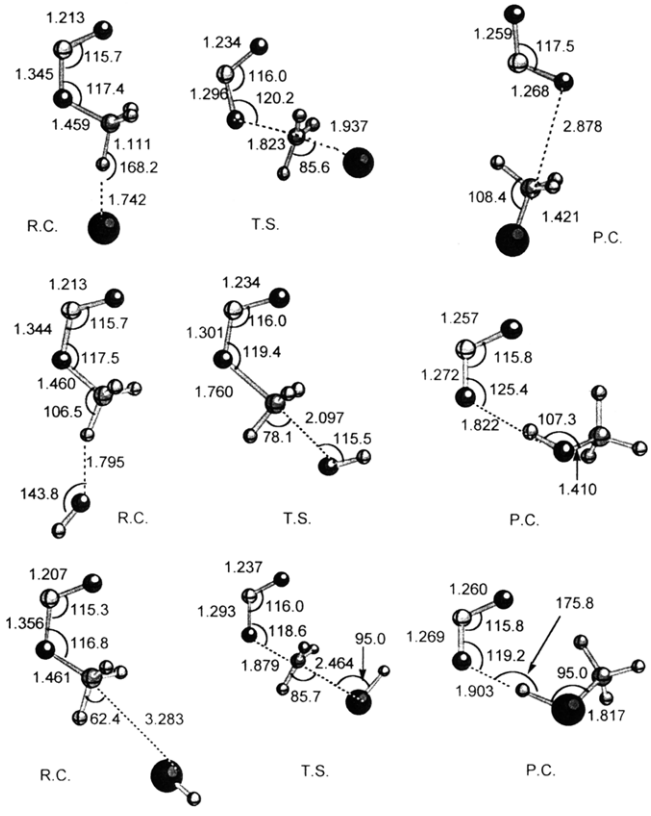


Figure 2-1. Geometries of reactant complexes, transition states and product complexes in S_N2 Reactions of methyl nitrite.

expulsion required in the TS with the weaker bases (for methyl (ethyl) nitrite bond cleavages in the TS are 37% (15%) and 48% (50%) for OH^- and SH^- respectively). In general, the stronger the base, the earlier is the TS on the reaction coordinate (smaller $\%\Delta n^{\neq}$ for r_2) and the lower is the activation barrier, in agreement with the Bell-Evans-Polanyi (BEP) principle.[10] The activation free energies, $\Delta G^{\neq}$, for the ethyl nitrite reactions are slightly higher by 1~4 kcal mol^{-1} than the corresponding reactions with methyl nitrite. The degrees of bond formation and bond cleavage in the TS (Table 2) are, however, quite similar (except for OH^-) so that the lower reactivity *i.e.*, higher $\Delta G^{\neq}$, of the ethyl series may be ascribed to the steric hindrance in the bond formation of the nucleophile in the TS.

Elimination Reactions:

A) Reactions of SH^- and F^- with methyl nitrite: The gas-phase elimination reactions of methyl nitrite with the two weaker bases, SH^- and F^-, are found to proceed through double-well potential energy surfaces (Figure 1). The elimination reactions are, however, highly endothermic ($\Delta G^o \gg 0$) in contrast to the large exothermicity found for the S_N2 processes. The high product levels ($H_2S + CH_2O + NO^-$ and $HF + CH_2O + NO^-$) can be, and indeed found to be, lowered by the formation of long lived collisional complexes of NO^- and HF (NO^- and H_2S in the case of $B^- = SH^-$) in which HF vibrationÅ*ESFqN=qMP=M=SKSNU=NRMKUUN=q*MKMNO=qÅ*xE)FOREiFKNTMN*EFq*LqOO=N=q*NMKO=M=M=NMKO

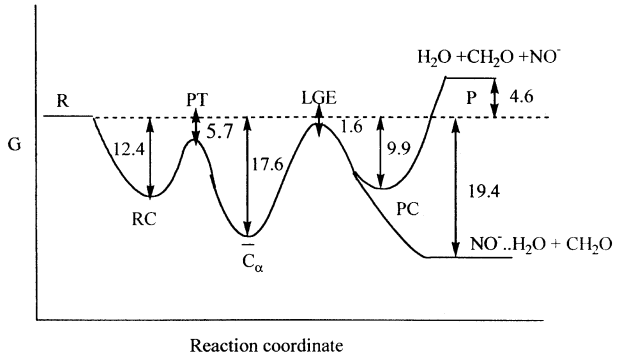


Figure 3. The free energy profile for the elimination reaction of CH_3ONO with OH^-. PT: Proton transfer, LGE: Leaving group expulsion

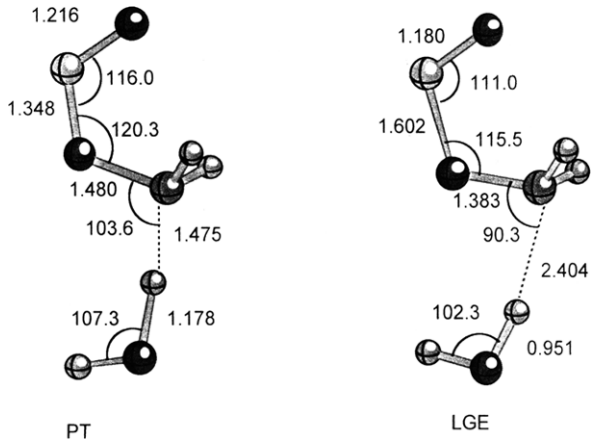


Figure 4. Geometries of stationary points (PT and LGE) for eliminations reaction of methyl nitrite.

the E1cb pathway. The first energy barrier corresponds to the proton transfer step (PT) and after the carbanion C_α^- formation leaving group expulsion (LGE) occurs in the rate-limiting step. This reaction thus proceed by an irreversible E1cb process.[12] This reaction is exothermic and can proceed efficiently with negative activation energy of 5.7 kcal mol^{-1}. The MP2/6-311+G* structure of the two stationary points (PT and LGE) are shown in Figure 4.

a) β-Elimination reactions of ethyl nitrite: The elimination reactions of ethyl nitrite induced by β-proton abstraction proceed by an E2 mechanism through a typical double-well free energy profile with all the bases, SH^-, F^- and OH^-. Exothermicities ($-\Delta G^\circ$) of the reaction increase with the PA of the bases, $-\Delta G^\circ$: $SH^- < F^- \ll OH^-$. The TS becomes later along the reaction coordinate and the barrier height ($\Delta G^{\neq}$) increases as the PA of base decreases, Table 3.

The β-proton abstraction leads to a β-carbanion, C_β^-, in which $n_{C\beta}$-σ^*_{CO} charge transfer interaction is much stronger than the $n_{C\alpha}$-σ^*_{ON} interaction encountered in the α-proton abstraction. This is due to the strong polar atom O relative to C in the σ^*_{CO} orbital. It has been shown that the intrinsic acceptor ability of C-X bond is in the order C-F > C-O > C-N > C-C $\gg$ O-N.[7] Results of the vicinal n-σ^* type charge transfer interaction are to weaken the σ^* (C-O) bond and strengthen the intervening (C_β-C_α) bond.[6,7] As a result, the MP2/6-311+G* geometries show that C_α-O bond becomes stretched (or weakened) from 1.446 Å in the substrate to 2.394 Å in the β-carbanion facilitating the leaving group departure in the TS. The lower activation energies, $\Delta G^{\neq}$, of β-elimination than the α-elimination of methyl nitrite (Table 3) should result partly from this efficient n-σ^* charge transfer interaction in the β-carbanion.

b) α-Elimination reaction of ethyl nitrite: Our results show that the elimination reaction of ethyl nitrite induced by α-proton abstraction ($E_{CO}2$ path in Scheme 1) proceeds only with a strong base, OH^-. The proton-transfer energies (Table 1) reveal that the α-proton abstraction is exothermic ($\delta\Delta G^\circ < 0$) only with OH^-. This is consistent with the gas-phase experimental results of DePuy and coworkers[3] who found that the reaction of F^- with ethyl nitrite forms exclusively NO_2^-, implicating either an S_N2 or β-elimination mechanism with no α-elimination product, NO^-. The α-proton transfer energy is exothermic ($\delta\Delta G^\circ < 0$) only with OH^- ($\delta\Delta G^\circ \cong$ -0.3 kcal mol^{-1}) and for F^- it is *ca.* 18 kcal mol^{-1} higher than this ($\delta\Delta G^\circ \cong 18$ kcal mol^{-1}). On the other hand, the α-proton transfer from ethyl nitrite to F^- requires much higher energy than the β-proton transfer (by *ca.* 36 kcal mol^{-1}) so that the α-elimination reaction of ethyl nitrite with F^- can not compete with the β-elimination pathway (and also with the S_N2 path). A triple-well free energy profile for the α-elimination of ethyl nitrite with OH^- (Figure 5) is quite similar to that for the α-elimination of methyl nitrite (Figure 3). For the α-elimination of ethyl nitrite both the activation ($\Delta G^{\neq} < 0$) and reaction energies ($\Delta G^\circ < 0$) are negative so that the α-elimination of ethyl nitrite should be a more facile process in the gas phase than that of methyl nitrite. Comparison of activation barriers, $\Delta G^{\neq}$, in Table 3 shows that α-elimination of ethyl nitrite can compete with β-elimination albeit the latter path is much more exothermic ($\Delta G^\circ = -40.1$ *vs* -20.2 kcal mol^{-1}) so that it is thermodynamically much more favorable.

In summary, both substrates, methyl and ethyl nitrites, can react with all the anionic nucleophiles, SH^-, F^- and OH^-, in the gas phase through S_N2 channels with relatively low activation barriers ($\Delta G^{\neq} = -2.1 \sim -15.4$ kcal mol^{-1}) in highly exothermic processes ($\Delta G^\circ = -19 \sim -76$ kcal mol^{-1}). The strongest base, OH^-, can induce both α-(methyl and ethyl nitrites) and β-elimination (ethyl nitrite) reactions. The α- and β-elimination channels of ethyl nitrite with OH^- are competitive with similar activation barriers ($\Delta G^{\neq} \cong$ -5 kcal

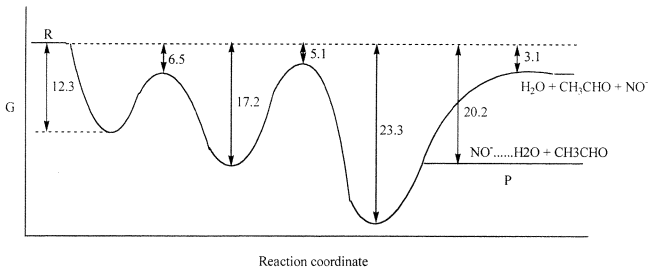


Figure 5. Free energy profile for the α–elimination reaction of ethyl nitrite with OH^-.

mol^{-1}). These elimination channels are slightly more favorable than the S_N2 channel ($\Delta G^{\neq}$ = -1.0 kcal mol^{-1}). The α-elimination of methyl nitrite with F^- is enabled by the complexation ($\Delta H_{comp} \cong$ -20 kcal mol^{-1}) between carbanion ($^-CH_2ONO$) and HF, which provides a rather stable intermediate within a triple-well energy profile of E1cb mechanism.

Acknowledgment. We thank Inha University and MOST/STEPI for support of this work. One of us (Park, H. Y.) also thanks for a university postdoctoral position.

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