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Theoretical ab Initio Study of Nucleophilic Substitution Reactions Involving Radical Anion Intermediates

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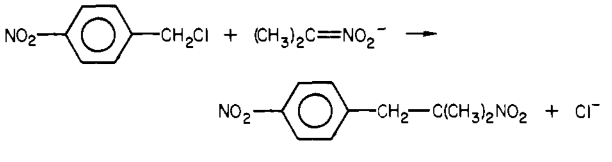
Abstract: The mechanism of nucleophilic substitution reactions which proceed via radical intermediates, as N. Kornblum proposed for the first time 16 years ago, is investigated by theoretical ab initio calculations.[1] The proposed mechanism involves electron transfer from an anion (or radical anion) to a neutral molecule and dissociation of the radical anion to an anion and a radical. The system studied here concerns the reactants $CH_2NO_2^-$ and $ClCH_2NO_2$. The study shows that the radical anion $ClCH_2NO_2^{-}\cdot$ cannot be considered as an intermediate species, since it dissociates spontaneously to Cl^- and $CH_2NO_2\cdot$. The present paper emphasizes the electronic requirements of such a fragmentation which could represent a key factor of the overall process. The influence of solvation is analyzed via the electrostatic model of Stillinger and Rahman with water molecules.

In the fifties, Kornblum et al.[2] undertook a study of substitution reactions of organic halides by nucleophilic species such as $CR_2{=}NO_2^-$. In order to explain the strong influence of the structural properties of the alkyl halide on the distribution of substituted products (O- or C-alkylation)[3] and on the rate of the reactions,[4a] this group suggested, in 1964, that C-alkylation of the nitroparaffin salt involves neutral and anionic radical species.[4b] Two years later, a sequence of elementary chain reaction steps was simultaneously proposed by Kornblum et al.[5a] and Russell et al.[6] to describe the mechanism. The intervention of radical species in a substitution reaction involving nucleophilic reagents and polar solvents stood for a very fresh hypothesis, since the now classical mechanisms of nucleophilic substitution reactions—S_N1, S_N2—were already firmly established. Kornblum showed that the O-alkylated product was the result of a S_N2 reaction path while C-alkylation followed the new radical mechanism he suggested.

These facts were clearly demonstrated by the study of the reaction involving *p*-nitrobutyl chloride and 2-nitropropyl anion (eq 1), for example.



(1)

The proposed mechanism involves, besides an initiation step A, a propagation sequence with three steps B, C, and D:

$$RX + Y^- \rightarrow RX^{-}\cdot + Y\cdot \tag{A}$$

$$RX^{-}\cdot \rightarrow R\cdot + X^- \tag{B}$$

$$R\cdot + Y^- \rightarrow RY^{-}\cdot \tag{C}$$

$$RY^{-}\cdot + RX \rightarrow RY + RX^{-}\cdot \tag{D}$$

The elementary steps A and D involve electron transfer from an anion or a radical anion to a neutral molecule and thus lead to the formation of a new radical anion; the steps B and C correspond to the dissociation and the formation of a radical anion, respectively. The sum of the steps B, C, and D represents the real link of the chain mechanism, since the radical anion $RX^{-}\cdot$ produced in step D is consumed in step B.

The initiation step A here considered is thermally induced. However, the electron transfer to which it corresponds can be induced by other means:[4] photochemical excitation or electro-

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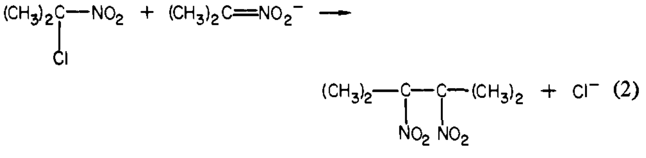
chemical[7] or chemical reduction.

The electron-transfer mechanism occurs mainly when X is a poor leaving group in a classical S_N2 mechanism. Thus, such a mechanism corresponds to a particularly useful synthetic tool with respect to substrates which do not react by the classic substitution methods.[5] It concerns not only aliphatic sites with one of the substituents which is either an appropriate aromatic group[3,8] or a nitro group NO_2,[9] but also aromatic sites.[10]

The simplest reactants whose transformation has been experimentally observed according to the presently studied mechanism are 2-chloro-2-nitropropane and 2-nitropropyl anion (eq 2):[9]



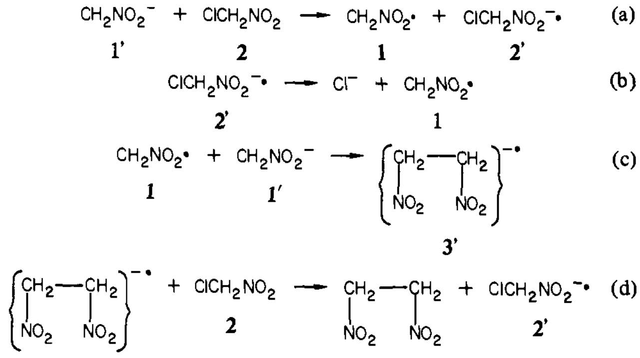
$$(CH_3)_2\underset{\displaystyle Cl}{C}{-}NO_2 + (CH_3)_2C{=}NO_2^- \longrightarrow (CH_3)_2{-}\underset{\displaystyle NO_2}{C}{-}\underset{\displaystyle NO_2}{C}{-}(CH_3)_2 + Cl^- \quad (2)$$

2

Description of the Study. Experimentally, several arguments strongly support the view that radical species are involved in the considered reactions. Thus, it may appear valuable to undertake a theoretical quantum mechanical study of the proposed mechanism in order to answer some of the following questions: are aliphatic radical anions stable chemical species or are they only transition state species? What are the factors which determine their stability? What are the structural, thermodynamic, and electronic features required by the substrates involved in the mechanism in order for the reaction to be efficient? How does the electron transfer proceed? What are the limiting steps among the elementary steps B, C, and D?

In order to approach these questions with the means of ab initio calculations, it is of importance to have a model which could correctly describe the experimentally reacting substrates. The simplest model satisfying this requirement is constituted by the nitromethyl anion $CH_2NO_2^-$ and chloronitromethane, $ClCH_2NO_2$. It differs from the aliphatic system (eq 2) above mentioned only by the substitution of the methyl groups by hydrogen atoms.

Accordingly, the following steps have been studied:



$$\underset{\mathbf{1'}}{CH_2NO_2^-} + \underset{\mathbf{2}}{ClCH_2NO_2} \longrightarrow \underset{\mathbf{1}}{CH_2NO_2\cdot} + \underset{\mathbf{2'}}{ClCH_2NO_2^{-}\cdot} \quad \text{(a)}$$

$$\underset{\mathbf{2'}}{ClCH_2NO_2^{-}\cdot} \longrightarrow Cl^- + \underset{\mathbf{1}}{CH_2NO_2\cdot} \quad \text{(b)}$$

$$\underset{\mathbf{1}}{CH_2NO_2\cdot} + \underset{\mathbf{1'}}{CH_2NO_2^-} \longrightarrow \underset{\mathbf{3'}}{\left\{\underset{\displaystyle NO_2}{CH_2}{-}\underset{\displaystyle NO_2}{CH_2}\right\}^{-\cdot}} \quad \text{(c)}$$

$$\underset{\mathbf{3'}}{\left\{\underset{\displaystyle NO_2}{CH_2}{-}\underset{\displaystyle NO_2}{CH_2}\right\}^{-\cdot}} + \underset{\mathbf{2}}{ClCH_2NO_2} \longrightarrow \underset{\mathbf{3}}{\underset{\displaystyle NO_2}{CH_2}{-}\underset{\displaystyle NO_2}{CH_2}} + \underset{\mathbf{2'}}{ClCH_2NO_2^{-}\cdot} \quad \text{(d)}$$

First, let us note that in this particular reaction, the nucleophilic reactant Y^- ($CH_2NO_2^-$) is identical with the aliphatic group R of the substrate RX. The energetic profile of reactions b and c, which are associated with simple variations of nuclear coordinates, have been studied by the classical procedures of determination of potential surfaces by ab initio calculations. The reactions a and d correspond to electron transfers which are not directly related to nuclear motions. It is usually estimated that the rate of the so called electron transfer is very large compared with the rate of approach of the reactants.[11] Accordingly, in a first step, we have restricted ourselves to determining the geometrical and electronic structures and relative energies of the initial and final states of reactions a and d. In a second step, we have simulated the electron transfer with perturbational method.

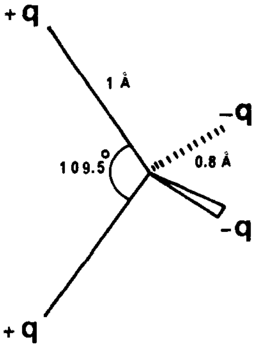


Figure 1. ST2 model for water molecule. $q = 0.2357$ a.u.

Calculation Methods. Ab initio calculations have been performed with use of the GAUSSSIAN 70[12a] program. The closed shell and doublet spin shell systems are described by Roothaan[13] and restricted Nesbet[14] procedures, respectively. It is clearly established that if neutral or positively charged molecular species are correctly described by using basis sets of reduced dimension (i.e., STO-3G[12b] or 4-31G[12c] basis sets), anionic species require the use of basis sets including polarization functions.[15]

As far as we are concerned, we chose to use one basis constituted by adding four (one s, three p) polarization functions on each atom, except hydrogen, to the minimal basis set, STO-3G.[12b] This choice is suggested by the size of the molecular systems we have to calculate in connection with the limits of our computational means. Every polarization function is developed on a set of three Gaussian functions, whose exponents are optimized with respect to total molecular energy by the "scale factor"[12a,16] procedure. We will go back into the details of this problem when the calculations relative to structural properties are reported.

Once the SCF step terminated, a CI calculation involving a few hundred mono- and biexcited configurations is performed.[12d] This CI segment aims to describe the dissociative step satisfactorily.

The ab initio calculations mentioned above describe molecular systems without interaction with the surrounding medium. In order to determine the solvent effects on the ab initio results, a simple method to estimate the solvtion enthalpy ΔH_{sol} has been used. This method, purely electrostatic (interaction between point charges), is based on Stillinger and Rahman's model ST2.[17] For the sake of simplicity, water has been elected to represent a polar solvent.

Let us recall the principle of this method as it has been used by Karplus et al.,[18] for example. Every molecule of water is described by four point charges located inside a Lennard-Jones' sphere. The positive charges are located on the hydrogen atoms and the two negative charges are located in sites representative

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[16] Every S or P polarization orbital Ψ is represented by three Gaussian functions: $\alpha_1 = 0.483$, $C_1^S = -0.2196$, $C_1^P = 0.01059$; $\alpha_2 = 0.1347$, $C_2^S = 0.2256$, $C_2^P = 0.5952$; $\alpha_3 = 0.0527$, $C_3^S = 0.9004$, $C_3^P = 0.4620$, with $\Psi = \sum \xi^{3/2} C_i \exp(-\alpha_i \cdot \xi^2 \cdot r^2)$ (ξ is the scale factor).

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Table I. Values of Lennard-Jones Parameters Used in the Present Study[18]

	ϵ, kcal/mol	σ, Å
C	0.09	3.208
H	0.00449	2.616
N	0.1600	2.770
O	0.2304	2.640
Cl	0.400	3.400

of the oxygen lone pairs (Figure 1). The various interaction terms the calculations have to take into account correspond, on the one hand, to interactions between water molecules and, on the other hand, to interactions between the atoms of solute and water molecules.

The former interactions are described by a potential function $V_{W_1W_2}$ defined as follows:

$$V_{W_1W_2} = 4\epsilon_W\left[\left(\frac{\sigma_W}{r}\right)^{12} - \left(\frac{\sigma_W}{r}\right)^{6}\right] + \sum_{i=1}^{4}\sum_{j=1}^{4}\frac{q_i^{W_1}q_j^{W_2}}{r_{ij}}S(r)$$

$$S(r) = 0 \qquad \text{if } 0 < r < R_L$$

$$S(r) = \frac{(r - R_L)^2(3R_U - R_L - 2r)}{(R_U - R_L)^3} \qquad \text{if } R_L < r < R_U$$

$$S(r) = 1 \qquad \text{if } r > R_U$$

$R_L = 2.016$ Å, $R_U = 3.129$ Å, $\epsilon_W = 0.07575$ kcal/mol, $\sigma_W = 3.10$ Å, $q_i^{W_1}$ represents one of the four charges of the water molecule 1, r represents the intermolecular distance between the oxygen atoms of water molecules 1 and 2, and r_{ij} represents the distance between the charges $q_i^{W_1}$ and $q_j^{W_2}$.

The latter interactions between solute and solvent are described by a potential function $V_{W\text{-}S}$ defined as follows:

$$V_{W\text{-}S} = \sum_{\lambda}\left[4(\epsilon_\lambda\epsilon_W)^{1/2}\left[\left(\frac{\bar{\sigma}_\lambda}{r_{0\lambda}}\right)^{12} - \left(\frac{\bar{\sigma}_\lambda}{r_{0\lambda}}\right)^{6}\right] + \sum_{i=1}^{4}\frac{q_i^W q_\lambda}{r_{i\lambda}}\right]$$

with $\bar{\sigma}_\lambda = (\sigma + \sigma_W)/2$. σ_λ and ϵ_λ, on the one hand, and q_λ, on the other hand, are the parameters of Lennard-Jones potential functions and the electrostatic potential function of atom j of the solute molecule, respectively. The values of q_λ are determined by ab initio calculations of Mulliken populations. The values of ϵ_λ and σ_λ are given in Table I.

Ab Initio Calculations on Reactants and Products. The molecular species considered are Cl^-, $CH_2NO_2^-$, $CH_2NO_2\cdot$, $ClCH_2NO_2$, $ClCH_2NO_2^-\cdot$, NO_2CH_2–CH_2NO_2, and $NO_2CH_2CH_2NO_2^-\cdot$. The details of the study relative to these compounds are analyzed in the next sections.

1. Cl^-. The chloride anion has already been studied plentifully by ab initio methods.[20] In the present study, the basis set used (STO-3G + 4 polarization orbitals s and p[16]) gives an energy of −454.7232 a.u. ($\xi = 1.0$) for the anion and of −454.6168 a.u. for the radical. An electronic affinity for atomic chlorine of +2.9 eV is deduced. Let us recall that the most reliable experimental value is +3.6 eV.[19] This value is in excellent agreement with the ab initio value (+3.53 eV) determined by Clementi et al.,[20] using a correction for correlation energy. The HF limit is estimated to be +2.58 eV[21] while calculations with the STO-3G basis set supply a value of −1.36 eV. The comparison of the last values with the values determined in this study shows that the addition of polarization orbitals to the STO-3G basis set gives a correct description of the anion.

2. $CH_2NO_2^-$, $CH_2NO_2\cdot$. The anion $CH_2NO_2^-$ has already been calculated by various authors.[22,23] Here, the planar STO-3G optimized structure has been assumed. The calculated dipole moment of $CH_2NO_2\cdot$ in the above-mentioned geometry is larger than 4 D. Thus, Crawford's theorem[24] enforces a positive electronic affinity for this species. Various basis sets have been used to calculate its value. The results are shown in Table II.

Table II. Energies of $CH_2NO\cdot$ and $CH_2NO_2^-$ as a Function of the Basis Set[a]

basis set	$E(CH_2NO_2^-)$, a.u.	$E(CH_2NO_2\cdot)$, a.u.	EA, eV
STO-3G	−239.6672	−239.7425	−2.05
4-31G	−242.69168	−242.6102	2.22
STO-3G[b]	−240.0913	−240.0307	1.65
STO-3G[c]	−240.1400	−240.0657	2.02
STO-3G[d]	−239.7985	−239.8082	−0.27
STO-3G[e]	−240.1638	−240.0681	2.60
STO-3G[f]	−240.1751	−240.0794	2.61

[a] All the scale factors have been optimized. They are roughly constant whatever the basis: $\xi_C = 1.0$; $\xi_O = 1.2$; $\xi_N = 1.1$. [b] With polarization functions on oxygen atoms. [c] With polarization functions on nitrogen and oxygen atoms. [d] With polarization functions on carbon atoms. [e] With polarization functions on carbon and oxygen atoms. [f] With polarization functions on carbon, nitrogen, and oxygen atoms.

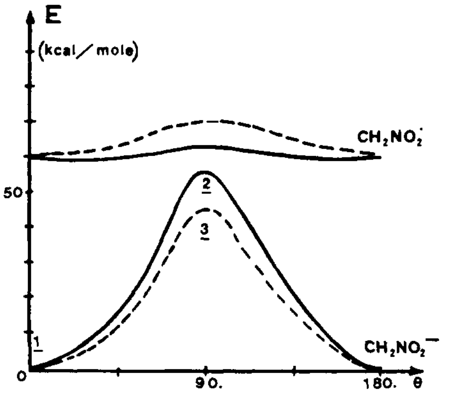

Figure 2. Potential energy curves relative to the nitromethyl radical $CH_2NO_2\cdot$ and nitromethyl anion $CH_2NO_2^-\cdot$ during the rotation of the CH_2 group about the CN bond. The full and dashed lines correspond to the rotation without or with pyramidalization of the methylene group, respectively. 1 refers to the planar structure and 2 and 3 to the perpendicular twisted structures with and without bending of the methylene grouping, respectively.

They emphasize that, if there are already polarization functions on oxygen and carbon atoms, addition of other polarization functions on the nitrogen atom does not modify the electronic affinity significantly. This result is easily read if resonance structures are drawn (nitrogen atom is positively charged) and confirms Benioff's work on NO_2^-.[25] It has been checked that the addition of polarization functions on the hydrogen atoms does not modify the value of the electronic affinity. These results bring us along to keep the following basis set for the subsequent calculations: the STO-3G basis + polarization functions on every oxygen and carbon atom. The SCF calculated value for the electronic affinity of $CH_2NO_2\cdot$ is +2.6 eV. To the best of our knowledge, only an approximate experimental value of +0.5 eV is reported in the literature.[26] Let us note that a CI calculation involving all mono- and biexcited configurations of the π system of $CH_2NO_2^-$ and $CH_2NO_2\cdot$ gives a value of +2.5 eV.[27]

The rotation about the CN bond of $CH_2NO_2^-$ and $CH_2NO_2\cdot$ has been studied. The corresponding potential energy curves are depicted in Figure 2. The geometries previously determined by

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(27) The absolute calculated values of energies are $E(CH_2NO_2^-) = -240.22068$ a.u. and $E(CH_2NO_2\cdot) = -240.130068$ a.u.

Table III. Variation of Atomic Charges of $CH_2NO_2^-$ during the Twisting of the Molecule

	$CH_2NO_2^-$	
atom	planar[a]	staggered, pyramidalized[a]
C	−0.36	−0.68
N	0.15	0.19
O_1	−0.52	−0.32
O_2	−0.52	−0.39
H	0.13	0.10

[a] Atomic charges in a.u.

Csizmadia et al.[22] have been assumed for the staggered (**2**) and pyramidalized (**3**) forms. For the anion, these forms are situated at 55 and 43 kcal/mol, respectively, above the planar structure (**1**) and do not correspond to stable structures. The rotation and pyramidalization lead to a strong modification of the charge distribution as shown in Table III. The negative charge initially localized on the oxygen atoms of the NO_2 group is shifted to the carbon atom.

3. NO_2CH_2–CH_2NO_2 and NO_2CH_2–$CH_2NO_2^{-}\cdot$. The basis set presently used is the same as that used in the study of $CH_2NO_2^-$ and $CH_2NO_2\cdot$. Standard geometrical parameters[28] have been assumed without further optimization. The calculated energies for the neutral molecule and the radical anion of 1,2-dinitroethane are −480.2571 a.u. and −480.2654 a.u., respectively. It leads to an electronic affinity of +0.22 eV for NO_2CH_2–CH_2NO_2. By using these results and those of the former section, the CC bond energies of the neutral molecule and the radical anion are obtained: $\Delta H_{CC}(NO_2CH_2\text{–}CH_2NO_2)$ = 76 kcal/mol; $\Delta H_{CC}(NO_2CH_2\text{–}CH_2NO_2^{-}\cdot)$ = 21 kcal/mol.

4. $ClCH_2NO_2$ and $ClCH_2NO_2^{-}\cdot$. The structure (S_1) of the neutral molecule has been determined at the STO-3G level. All the bond lengths have been optimized[29] while keeping all the bond angles fixed to their standard value, (HCCl,NCCl,HCH) = 109.5°, (ONO) = 120.0°. The nitro group NO_2 is assumed to be orthogonal to the NCCl plane (S_1 = staggered structure). The STO-3G and STO-3G + polarization functions calculated energies are −694.4052 a.u. and −694.7732 a.u., respectively. The scale factor of polarization functions has been determined with the radical anion: $\xi_C = 1.1$, $\xi_O = 1.2$, $\xi_{Cl} = 1.0$. The calculated energies of the radical anion are −694.2654 a.u. (STO-3G basis set) and −694.7988 a.u. (STO-3G + polarization functions basis set). The resulting vertical electroaffinity of $ClCH_2NO_2$ is −3.8 eV at the STO-3G level and +0.70 eV at the extended basis set level.

An exploratory study of the geometry of the radical anion shows that the lengths of bonds NO, CN, and CH have an energetic minimum while the Cl bond does not. This finding leads us to undertake a study of the dissociation of $ClCH_2NO_2^{-}\cdot$ to $CH_2NO_2\cdot$ and Cl^-.

Calculations previously published by Salem et al.[30] on the $CH_3Cl^{-}\cdot$ and by Buenker and Peyerimhoff[31] on $CF_3Cl^{-}\cdot$ show that, in the first case, the dissociation requires an activation energy of 16 kcal/mol, while in the second case, it is spontaneous and exothermic.[32]

In order to analyze the rupture of the C–Cl bond of chloronitromethane, calculations with extended basis set and CI[33] have been performed. The reaction coordinate is the distance between the carbon and chlorine atoms. In each point, the other geometrical parameters have been optimized. The resulting potential energy curves relative to the dissociation of $ClCH_2NO_2^-$ and $ClCH_2NO_2^{-}\cdot$ are depicted in Figure 3. They show that the rupture of the C–Cl bond of $ClCH_2NO_2$ requires an energy of 68 kcal/mol corresponding to the endothermicity of the reaction, but that the rupture of the radical anion $CH_2NO_2Cl^{-}\cdot$ is spontaneous and exothermic (ΔH = −17 kcal/mol).

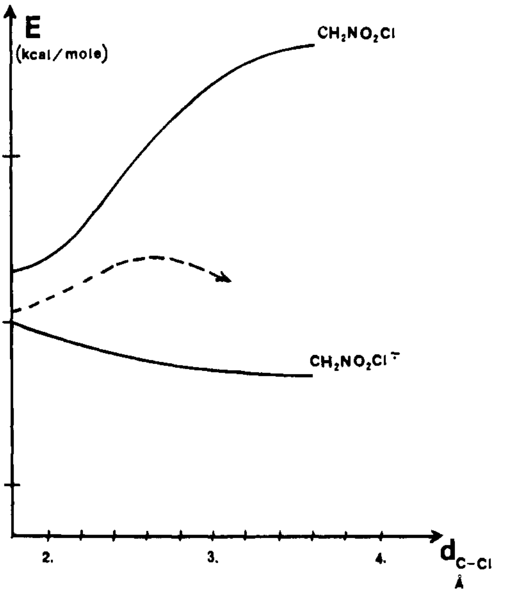

Figure 3. Potential energy curves relative to $ClCH_2NO_2$ and $CH_2NO_2Cl^{-}\cdot$ during the lengthening of the C–Cl bond. The dashed lines correspond to the radical anion $ClCH_2NO_2^{-}\cdot$ in its NO_2–Cl eclipsed configuration.

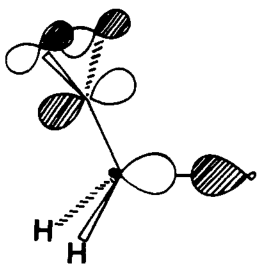

Figure 4. Lowest unoccupied (LUMO) orbital of $ClCH_2NO_2$. It corresponds to an in-phase mixing of the π antibonding orbital of NO_2 with the σ antibonding of C–Cl.

It is interesting to try to determine the origins of the difference observed in the C–Cl rupture of the radical anions $CH_3Cl^{-}\cdot$ and $ClCH_2NO_2^{-}\cdot$, respectively. Salem et al.[30] consider that the barrier occurring in the dissociation of $CH_3Cl^{-}\cdot$ is due to the avoided crossing between the initially unoccupied orbital σ^*_{C-Cl} which correlates with the highest occupied orbital of Cl^- and the diffuse orbital mainly localized on carbon atoms which is initially occupied.

Figure 4 depicts the HOMO of the anion radical $ClCH_2NO_2^{-}\cdot$. It shows that it results from an in-phase mixing of the antibonding π orbital of the NO_2 group and of the antibonding orbital σ^*_{C-Cl}. Thus, when the C–Cl bond breaks, there is no crossing between occupied and unoccupied orbitals, but only a smooth reorganization of the latter which delocalizes from the NO_2 region to the C–Cl region with conservation of its phase properties. This interpretation is confirmed by the fact that when the CCl system concerns the eclipsed structure (S_2) of $ClCH_2NO_2^{-}\cdot$ (the NO_2 and NCCl groups lying in the same plane), a barrier is involved. Its height, which has not been determined as precisely as in the previous case, is larger than 10 kcal/mol. The preceding analysis leads us to conclude that the radical anion $ClCH_2NO_2^{-}\cdot$ is not a stable species. It dissociates spontaneously to Cl^- and $CH_2NO_2\cdot$ (reaction b).

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(28) Gordon, M.; Pople, J. A. *J. Am. Chem. Soc.* **1967**, *89*, 4253. r_{CC} = 1.54 Å, r_{CN} = 1.53 Å, r_{NO} = 1.28 Å.

(29) r_{CCl} = 1.77 Å, r_{CN} = 1.57 Å, r_{NO} = 1.28 Å, r_{CH} = 1.09 Å.

(30) Canadell, E.; Karafiloglou, P.; Salem, L. *J. Am. Chem. Soc.* **1980**, *102*, 855.

(31) Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys. Lett.* **1976**, *65*, 434.

(32) Both conclusions are at variance with experimental observations which suggest that the $CF_3Cl^{-}\cdot$ radical anion is stable in matrices at low temperatures (Hasegawa, A.; Shiotani, M.; William, F. *Faraday Discuss.* **1977**, *63*, 157) while $CH_3Cl^{-}\cdot$ is estimated to be an intermediate molecular species having only a transitory existence (Wentworth, W. E.; George, R.; Keith, H. *J. Chem. Phys.* **1969**, *51*, 1971. Fujita, Y.; Katsu, T.; Sato, M.; Takahashi, K. *Ibid.* **1974**, *61*, 4307).

(33) The CI involves all the mono and biexcited configurations built on the highest occupied and four unoccupied orbitals.

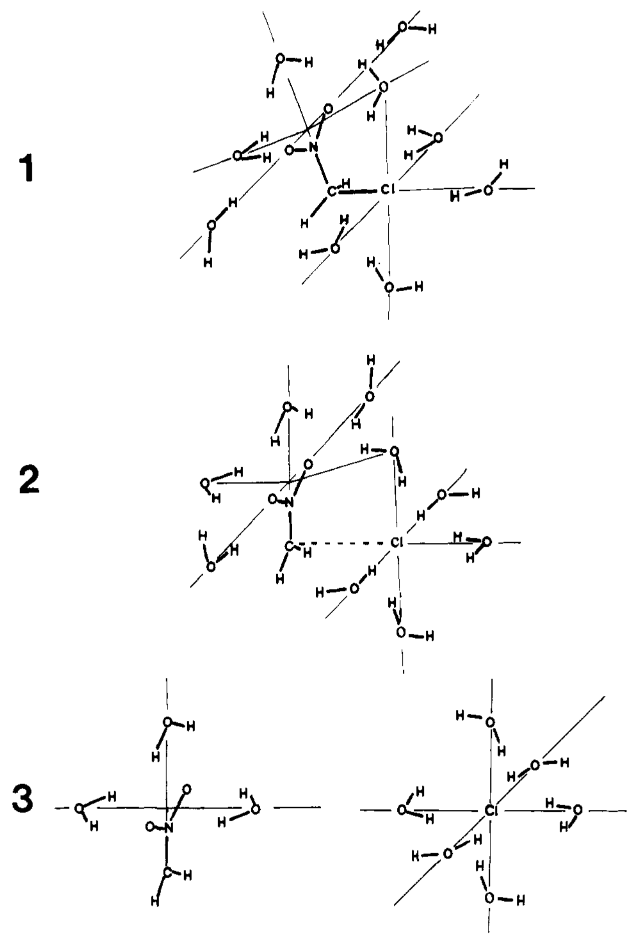

Figure 5. Schemes depicting the solvation shells of $ClCH_2NO_2^-$ during the C–Cl bond rupture for three values of r_{C-Cl}: 1.8 Å (1), 3.5 Å (2), 20 Å (3).

Thus, as far as steps a and b are concerned, $CH_2NO_2Cl^-\cdot$ is rather a transition-state structure than a reaction intermediate.

Solvation Effect. The solvation effect on the C–Cl system of $ClCH_2NO_2^-\cdot$ has been analyzed with the model previously described. Nine water molecules are surrounding the negatively charged systems. Their relative positions have been optimized in order to get the lowest energy. Figure 5 depicts the overall structure for C–Cl distances of 1.8 Å (initial point), 3.1 Å (intermediate point), 25 Å (final point).

The solvation energy of the initial, intermediate, and final systems are −73, −88, and −107 kcal/mol, respectively. The latter value corresponds to −87 kcal/mol for the Cl^- surrounded by six water molecules[34] and −20 kcal/mol for the radical $CH_2NO_2\cdot$ surrounded by three water molecules. Thus, the dissociation of the radical anion $ClCH_2NO_2^-\cdot$ is joined by a monotonous and exothermic variation of the solvation enthalpy of the system. (See Figure 3.) Once the various species intervening in the mechanism have been studied, let us consider each elementary step.

Mechanistical Study. Initiation Step e. This step corresponds to an electron transfer from the nitromethyl anion to the chloronitromethane molecule. Let us suppose that this transfer is fast compared to the life of a collision between the donor and the acceptor. The efficiency of the transfer is directly linked to the value of the interaction term between the HOMO orbital of the donor and the LUMO orbital of the acceptor and inversely proportional to the endothermicity of the reaction.[35a,36] The relative values of the interaction term for various approaches of the reactants can be estimated by using the Wolsberg–Helmholtz approximation.[35b] The HOMO–LUMO overlap has been determined in three special cases: parallel (case 1) or face to face (case 2) approaches of the nitro group of the donor and the acceptor in their most stable conformations, and face to face (case 3) approach to the nitro group of the acceptor in its most stable conformation (S_1) and of the methylene group CH_2^- of the donor in its staggered pyramidalized conformation. The approaches are considered only for distances d greater than the sum of Van der Waals' radii (about 3 Å). The curves $S = f(d)$ are depicted on Figure 6. They show that, at a distance of 3 Å, approach 3 corresponds to the largest interaction, HOMO–LUMO. Then approaches 2 and 1 follow in this order. The negative value of S observed in approach 1 for d larger than 3.5 Å is due to the out-of-phase overlap of the nitrogen–oxygen contributions which overbalances the in-phase overlap of the oxyen–oxygen contributions. As it has been previously mentioned, the most propitious conditions for the so called electron transfer correspond to, on the one hand, energetic positions of reactant system A (CH_2NO^{2-} + $ClCH_2NO_2$) and of product system B ($CH_2NO_2\cdot$ + $ClCH_2NO_2^-\cdot$) such that E_A is larger or equal to E_B, and, on the other hand, a maximal value of the $(HOMO)_{donor} - (LUMO)_{acceptor}$ overlaps.

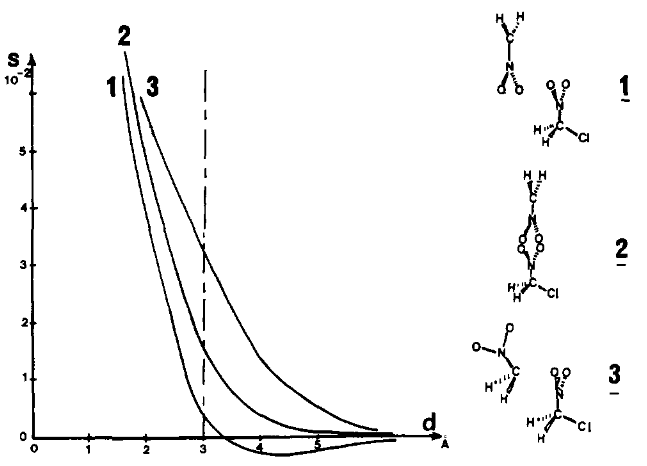

Figure 6. Overlap between the HOMO of $CH_2NO_2^-$ and the LUMO of $ClCH_2NO_2$ for the three different approaches 1, 2, and 3.

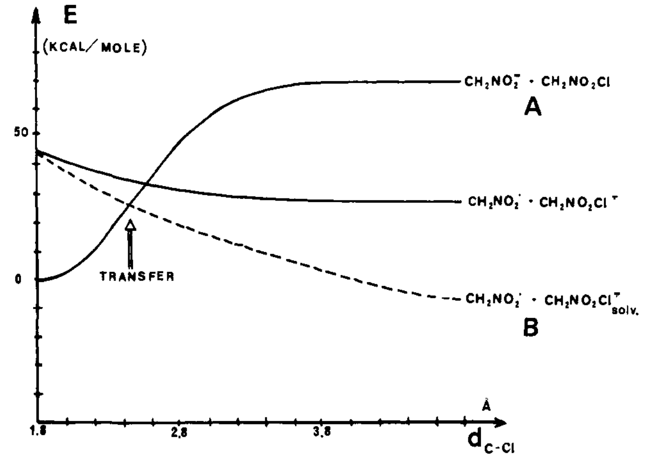

Figure 7. Potential energy curves relative to the systems A ($CH_2NO_2^-$ + CH_2NO_2Cl) and B ($CH_2NO_2\cdot$ + $ClCH_2NO_2^-\cdot$) as a function of the distance C–Cl. The dashed lines refer to the solvated systems.

Accordingly, two reaction paths could be considered to describe the initiation step a. The first corresponds to a rotation of the CH_2 group of the nitromethyl anion from the planar to the staggered pyramidalized conformation prior to transfer. The rotation has two results. On the one hand, it destabilizes system A and brings it to the energetic level of system B. On the other hand, it leads to an optimal HOMO–LUMO overlap during the approach of 3 of donor and acceptor. However, the large de-

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[34] Schuster, P.; Jakubetz, W.; Marius, W. *Top. Current Chem.* **1975**, *60*, 1.

[35] (a) Landau, L. D.; Lifshitz, E. M. "Quantum Mechanics"; Pergamon Press: New York, 1958; p 145. (b) Wolfsberg, M.; Helmholtz, L. *J. Chem. Phys.* **1952**, *20*, 835.

[36] Reynolds, W. L.; Larmry, R. W. "Mechanisms of Electron Transfer"; The Ronald Press Co.: New York, 1966.

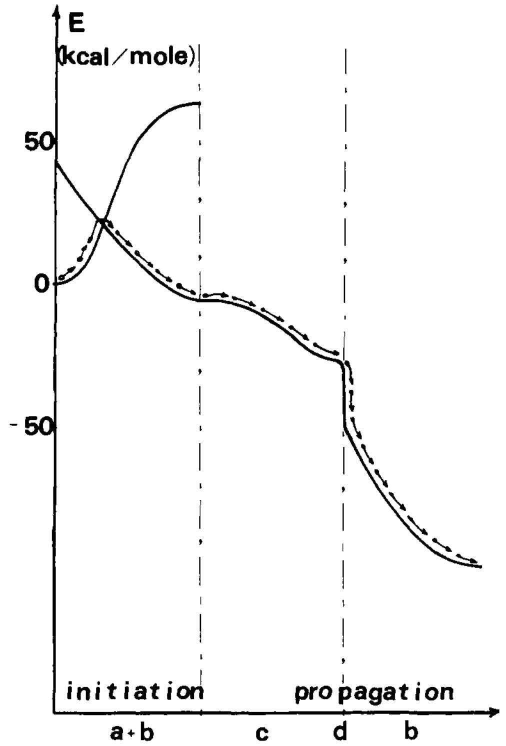

Figure 8. Potential energy curves for the sequence of steps a, b, c, and d.

stabilization associated with the twisting of the CH_2 group (+43.0 kcal/mol) makes this hypothetic reaction path very unlikely. The second reaction path which could be considered corresponds to a lengthening of the C–Cl bond of $ClCH_2NO_2$ prior to electron transfer during the approach of **2**. The lengthening does not destabilize system A as in the previously studied reaction path, but stabilizes system B. Thus, it reduces the energy gap associated with the vertical electron transfer (Figure 7). For a lengthening of 0.6 Å, both systems A and B are isoenergetic and are 25 kcal/mol above the most stable conformation of system A. Whatever the initial reaction path, once the electron transfer has occurred, the system dissociates spontaneously to $2CH_2NO_2\cdot$ + Cl^- by fragmentation of radical anion $ClCH_2NO_2^-\cdot$ (step b).

Propagation Steps. 1. Step c: $CH_2NO_2\cdot + CH_2NO_2^- \rightarrow NO_2CH_2\text{–}CH_2NO_2^-\cdot$. Step c is the formation of 1,2-dinitroethane from the nitromethyl radical and the radical anion. An exploratory SCF + CI calculation for this reaction path has been performed by using the minimal STO-3G basis set. The reaction coordinate is the distance between both methylene groups. A linear variation of the other geometrical parameters has been assumed. This preliminary calculation shows that the reaction requires no activation energy. By reason of the dimension of the extended basis set (68 orbitals), calculations with this basis have been performed only for the initial and final systems. They show that the reaction step c is spontaneous (no barrier for the same reasons as step b) and exothermic (−21 kcal/mol).

2. Step d. Step d is an electron transfer between the 1,2-dinitroethane radical anion and dichloronitromethane. The calculated electronic affinities of $NO_2CH_2CH_2NO_2$ and $ClCH_2NO_2$ are +0.22 and +0.7 eV, respectively. Accordingly, step d is exothermic (−12 kcal/mol). In such a case, electron transfer is fast (diffusion limited) as previously mentioned.[11] The most likely approach of the reactant could be similar to approach 2 which has been considered for step a. Figure 8 depicts the energetical variations associated with the set of reaction steps a, b, c, and h.

Conclusion

From this first theoretical ab initio study of the chain mechanism proposed by Kornblum and Russell to describe the nucleophilic substitution reaction involving radical and radical anions, the following results have been obtained.

(1) Radical anions of α-nitromonohaloalkyl derivatives with positive electroaffinity such as $ClCH_2NO_2^-\cdot$ are not stable species. They dissociate spontaneously to give the halo anion X^- and an α-nitro radical by rupture of the CX bond.[37]

(2) The spontaneity of the CX rupture is bound to the fact that, in the staggered conformation, the semioccupied orbital of the radical anion mixes greatly with the unoccupied antibonding orbital associated with the CX bond in an in-phase fashion. Broadly speaking, one can estimate a good feasibility of the dissociation of a radical anion every time the orbital which contains the unpaired electron mixes in-phase the antibonding σ orbital of the bond linking the carbon atom to the nucleofuge.

(3) The propagation rate of the chain (steps b, c, and d) of Kornblum's mechanism may be determined better by diffusion phenomena (steps c and d are bimolecular, but do not require activation energy) rather than by energetic considerations if the electron affinities of species **2** and **3** are in the same order as in the present study.

(4) It can be thought that anions such as $CH_2NO_2^-$ are poor nucleophiles for an S_N2 mechanism because the negative charge is very delocalized. Nevertheless, in their planar most stable conformation, more of the negative charge is on the oxygen atoms than on the carbon atom. This difference explains why the products of substitution by the S_N2 mechanism correspond to O-alkylation. A C-alkylation could be considered by the same S_N2 mechanism with the staggered pyramidalized conformation of the nucleophile $CR_2NO_2^-$. However, the present study shows that this conformation has a very high energy (+43 kcal/mol) and accordingly it has a very low probability of occurring.

(5) The driving force for electron transfer in the initiation step is the spontaneous dissociation of the radical anion $CH_2NO_2Cl^-\cdot$. The electron transfer could occur between the nitro groups of the donor and acceptor and require an activation energy of around 25 kcal/mol in a dipolar solvent. This value appears as a relatively high requirement if we consider the mild experimental conditions under which the reaction proceeds. However, one must keep in mind that usually the experimental nucleophile is not $CH_2NO_2^-$, but substituted derivatives such as $(CH_3)_2CNO_2^-$. The inductive donor methyl group must reduce the electron affinity of the nucleophile significantly and accordingly the energy barrier of steps a and b.[38]

In conclusion, let us emphasize the role of the nitro groups. On the one hand, they induce the spontaneous dissociation of the radical anion of the substrates NO_2CH_2X and, on the other hand, they are involved as relays in the electron transfer.

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(37) The present study is limited to α nitro-alkyl halides and emphasizes the determinant role played by the nitro group. Radical anions of other substituted halides, reacting according to Kornblum's mechanism, can be intermediate species. Experimentally, aromatic radical anions have been shown to have a measurable lifetime (10^{-1}–10^{-5} s) (see, for example: Mohamad, M.; Hadju, T.; Kosover, E. M. *J. Am. Chem. Soc.* **1977**, *93*, 1792. Bartak, D. E.; Hawley, M. D. *Ibid.* **1972**, *94*, 640. Neta, P.; Behar, D. *Ibid.* **1980**, *102*, 4798) while various non-nitro-alkyl halides are supposed to have a very short lifetime (10^{-6}–10^{-10} s) (see, for example: Anbar, M.; Hart, J. *J. Phys. Chem.* **1965**, *69*, 271; **1967**, *71*, 3700. Anbar, M. *Adv. Phys. Org. Chem.* **1969**, *7*, 115).

(38) The experimental influence of light[5b–d] or catalytic amount of NaH in Me_2SO[5d] on the reaction rate suggests that the initiation step RX + $CH_2NO_2^- \rightarrow R + X^- + CH_2NO_2\cdot$ could require a thermal activation larger than the mild conditions would let it suppose, in agreement with our calculations.