MNDO Study of Ring Opening in the Succinimidyl Radical

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Calculated (MNDO) activation barriers for ring opening of the π ground state and the low-lying σ excited state of the succinimidyl radical suggest that at room temperature only the latter can react in this way; the calculated lifetime of the σ radical agrees well with that estimated from kinetic studies.
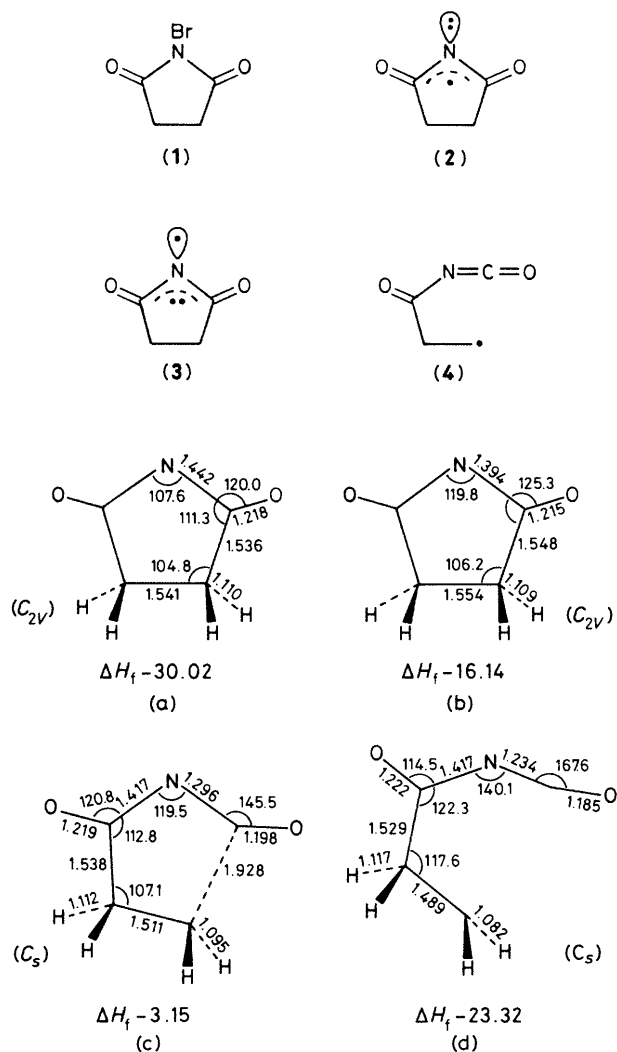
Skell et al.[1—4] have interpreted the reactions of N-bromosuccinimide (1) in terms of the existence of the succinimidyl radical in two orbitally isomeric forms, a π radical (2) with the unpaired electron in a π MO and a σ radical (3) with it in a σ MO. The former is assumed to be the lower in energy, in agreement with INDO calculations by Koenig and Wielesek[5] and e.s.r. studies by Lund et al.[6] While the difference in energy between (2) and (3) has not been determined, thermochemical arguments[4] set an upper limit of 20 kcal/mol.† MNDO and UMNDO calculations[7,8] predict the difference to be 13.8 and 14.6 kcal/mol, respectively, while a

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† 1 cal = 4.184 J.

Figure 1. Optimized geometries (bond lengths in Å, angles in degrees) and heats of formation (ΔH_f in kcal/mol) calculated for (a) (2); (b) (3); (c) the transition state for conversion of (3) into (4); (d) (4).

estimates of rate constants were based on erratic rate data, and that the assumptions they made were responsible for the conclusions they reached. The problem is clearly a very interesting one and merits further study. Here we report the results of some additional MNDO calculations designed to check two crucial points, *i.e.* ring opening in (2) and (3) and the lifetime of (3).

Previous MNDO[12] calculations[8] carried out here for (2) and (3) used the spin-unrestricted version (UMNDO[13]) of MNDO. However, when we studied their conversion into (4) using UMNDO we found that the overallowance[14] for electron correlation varied along the reaction paths, leading to substantial uncertainties in the activation barriers. To avoid this problem we first used UMNDO to locate stationary points along the minimum energy reaction paths. The stationary points were characterized by calculating and diagonalizing the Hessian matrix.[15] The relevant structures were then reoptimized using the 'half-electron'[14] (R.H.F.) version (MNDO-HE) of MNDO. The geometries obtained in this way were similar to those from UMNDO while the energies were 3—8 kcal/mol higher. The optimized geometries and heats of formation‡ calculated for (2), (3), and (4), and for the transition state for the ring opening of (3) to the ground state of (4), are shown in Figure 1. The transition state retains the symmetry plane containing the five main atoms and possesses C_s symmetry. The rearrangement of (3) to (4) is predicted to be exothermic by 7.2 kcal/mol, with an activation barrier of 12.9 kcal/mol and an activation entropy of 4.8 cal mol^{-1} K^{-1} at 25 °C. While no experimental value is available for comparison, the calculated activation parameters lead to a rate constant of 2.4×10^4 s^{-1} at 25 °C, which is quite close to the value (1.5×10^4 s^{-1}) estimated from kinetic data by Walling *et al.*[10] for the succinimidyl radical ring opening.

The conversion of (2) into (4) was next studied, using the length (R) of the breaking bond in (2) as the reaction co-ordinate. As expected,[5] this symmetry-forbidden pathway involved a continuous energy increase and led to a high-energy electronic state of (4). The calculated energy profile intersected the minimum energy reaction path obtained for the conversion of (3) into (4) at a point ($R = 1.845$ Å) 26.0 kcal/mol above (2). These results seem to suggest rather strongly that at ordinary temperatures the only succinimidyl radical that undergoes extensive ring opening is (3).

Finally, within the framework of the electric-dipole approximation[16] at NDDO level, we calculated the transition moment for the sponaneous decay of the excited state (3) of (1) to the ground state (2), finding it to be 0.0954 a.u. This low value leads to a calculated intrinsic emissive lifetime of 4.4×10^{-4} s, consistent with the estimate from kinetic data reached by Walling *et al.*[10] This long lifetime can in fact be very easily understood in terms of simple group theoretic considerations. In the C_{2v} symmetry group, the wavefunctions of (2) and (3) transform as the point group representations B$_1$ and A$_1$, respectively, so the transition moment between these states is predicted to be polarized along the molecular axis orthogonal to the ring plane. Since the SOMO of (3) is strongly localized in the hybrid sp^2 AO of nitrogen whereas the highest doubly occupied MO is a π MO delocalized over the 2p$_z$ AOs of

larger value (20.25 kcal/mol) has been estimated from an *ab initio* (STO-3G) study.[9] Skell *et al.*[1—4] based their conclusions on the different reactivities of succinimidyl radicals formed from (1) by removal of bromine by different kinds of radical. They concluded that only (3) can abstract hydrogen from other molecules or undergo spontaneous ring opening, leading ultimately to β-bromopropionyl isocyanate, the bromo compound corresponding to the radical (4).

Walling *et al.*[10] have recently criticized these conclusions on the grounds that the products formed do not always correspond to those predicted by Skell *et al.* and that their kinetic studies imply a rate constant for conversion into (4) of the species claimed to be (3) of $<2.1 \times 10^4$ s^{-1}, the values for hydrogen abstraction being even lower. If these estimates are correct, the lifetime of (3) must be $\sim 10^{-4}$ s^{-1}. This seemed to them unreasonably long, given that the $2\sigma \rightarrow 2\pi$ transition is not forbidden. Walling *et al.* suggest that the radical species described as (3) is neither (2) nor a bromine atom but some other species derived from (1) and Br.

Skell *et al.* have responded[11] to these criticisms by claiming that the experimental discrepancies were due to inadequate deoxygenation of solutions by Walling *et al.*, that their

‡ Note that the heats of formation calculated here for (2) and (3) are larger by 0.4 kcal/mol than the values reported by Clark.[7] This discrepancy is due to the fact that earlier versions of our MNDO program (*e.g.* W. Thiel, *Quantum Chemistry Program Exchange*, 1978, **11**, 353) had a rounding-off error in the one-centre exchange integrals and that the two-centre integrals (p$_x$p$_y$; p$_x$p$_y$) did not fulfil the correct symmetry relations between the appropriate Coulomb integrals. See W. Thiel, *J. Am. Chem. Soc.*, 1981, **103**, 1413.

nitrogen and oxygen, the only non zero component of the transition moment should clearly be very small.

While no current theoretical procedure can provide unequivocal answers in cases such as this,[17] the calculations reported here certainly support Skell's identification[11] of the species that undergoes ring opening as the $2\sigma \rightarrow 2\pi$ excited state (3) of (1) and the one that does not as the corresponding ground state, (2). In any case, no valid objections can be raised on the grounds that it leads to an unreasonable lifetime for (3).

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