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A theoretical study of the formation and destruction of the aci-forms of nitromethane and dinitromethane

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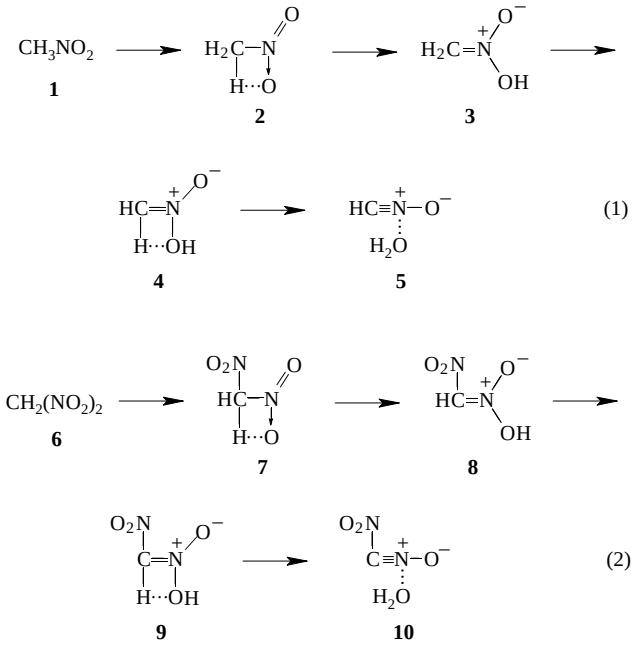
A quantum-chemical study of the dehydration mechanism of CH_3NO_2 and $CH_2(NO_2)_2$ molecules has shown that a water molecule eliminates from the respective aci-forms, formation of the latter being the limiting step of the whole process.

The study of tautomeric transformations is of substantial interest for the elucidation of general trends in the reactivity of aliphatic nitro compounds.[1,2] Various transformations of nitronic acids, in particular, those occurring during the thermal decomposition of nitroalkanes, are significant.[3-5] It has been reliably established[6] that the liquid-phase decomposition of nitromethane (NM) and nitroethane occurs *via* their aci-forms; evidently, the same is true for the gas-phase decomposition of NM at high pressures and at 600–800 °C, *i.e.* under supercritical conditions.[3,7] However, the kinetics and mechanisms of reactions of nitronic acids have not been adequately investigated. At present, this is a serious obstacle delaying the elucidation of the main trends in the thermal destruction of aliphatic C-nitro compounds in the liquid phase.[3,5] In a previous paper,[8] based on a MINDO/3 study of elementary steps in the unimolecular decomposition, we proposed a mechanism that included elimination of water from the aci-form of dinitromethane (DNM) and accounted for the low thermal stability and for the specific position of DNM in the series of nitroalkanes. However, the MINDO/3 method leads to substantial errors in the determination of the enthalpies of formation of NM and DNM. The enthalpies of formation of the aci-forms calculated in the study cited[8] were also too low, *i.e.* lower than those for NM and DNM, although the aci-forms do not exist in the gaseous phase as stable compounds.[1,2,8] In the case of NM, the barrier to the formation of the aci-form found by MINDO/3 (227 kJ mol^{-1}) differed markedly from that found by a non-empirical method (MP2/6-31G*//3-21G, 314 kJ mol^{-1}).[9] In view of the fact that the mechanism that we proposed[8] not only accounts for the long-known anomaly of DNM but is also of interest for understanding the mechanism of the unimolecular decomposition of nitro-compounds in the gaseous and condensed states, we performed an additional study of this process using non-empirical methods and the semi-empirical PM3 method. We studied elimination of water from the aci-forms of NM and DNM [reactions (1) and (2)].

A specific feature of this process is that it can occur in nitro-compounds with two or three hydrogen atoms at the α-position with respect to the nitro group and cannot occur in tri- or tetranitromethane.[8]

The non-empirical calculations were performed using the Dunning–Hays double Zeta valence basic Set[10] with inclusion of *d* polarising functions for heavy atoms (referred to below as DZV-1d). Full optimisation of geometrical parameters was carried out at the RHF level; after that, the electron correlation was taken into account using the second-order Meller–Plesset perturbation theory (MP2).[11] For the reaction of NM, the influence of higher-order correlation corrections [MP3, MP4(DQ)] was also estimated, and the results were compared with those obtained by the method of coupled clusters with allowance for double substitutions (CCD). The identification of the stationary points found for transition states (TS) was confirmed by the presence of one negative value in the Gesse matrix. For the processes involving NM, the correspondence of the TS found to the reactions in question was verified additionally by IRC-drops to the products. Non-empirical calculations were performed using GAMESS[12] and



GAUSSIAN-94 program (Rev B3). The semi-empirical PM3 calculations were carried out using the MOPAC program.[13] All the stationary points were calculated with an accuracy of 0.1 pm for bond lengths and 0.1° for bond and dihedral angles.

Some of the resulting data on the geometry of the reaction centres for the initial compounds and products of reactions (1) and (2) and for the corresponding TS are presented in Table 1. The main energy characteristics of these processes are given in Table 2.

The geometrical characteristics of the TS in the formation of NM and DNM, of the initial compounds and reaction products predicted by non-empirical and PM3 calculations are quite close. The main distinction is that according to PM3, the C–N O_2 bond in DNM is markedly longer than that in NM, which is in agreement with the main trends of the variation of

Table 1 Some geometrical parameters for the compounds and TS (*R*/pm) in reactions (1) and (2) found by non-empirical calculations.[a]

Structure	*R*(C–N)	*R*(N–O)	*R*(C–H)	*R*(O–H)
1	148.4 (151.4)	119.7 (121.4)	107.8 (110.1)	–
2	149.8 (143.0)	127.2 (130.6)	152.9 (159.5)	115.7 (121.8)
3	126.9 (130.7)	135.2 (144.1)	106.8 (108.7)	95.4 (95.6)
4	123.1 (123.1)	220.9 (187.5)	115.4 (137.5)	149.0 (141.6)
5 + H_2O	113.1 (116.6)	121.6 (121.1)	105.8 (107.0)	94.7 (95.2)
6	148.5 (154.8)	119.1 (120.7)	107.4 (111.7)	–
7	151.5 (146.2)	126.3 (129.2)	148.5 (110.9)	118.2 (130.7)
8	128.9 (133.3)	134.7 (142.6)	106.4 (110.9)	95.6 (95.7)
9	125.8 (125.3)	194.7 (182.1)	126.4 (142.0)	130.6 (138.4)
10 + H_2O	113.0 (117.6)	119.5 (120.7)	–	94.7 (95.1)

[a]Results found by the semi-empirical PM3 method.

Table 2 Barriers for the reactions (kJ mol^{-1}).[a]

Method	$\Delta H_{1,2}/(\Delta E_{1,2})$	$\Delta H_{1,3}/(\Delta E_{1,3})$	$\Delta H_{3,4}/(\Delta E_{3,4})$	$\Delta H_{3,5}/(\Delta E_{3,5})$	$\Delta H_{6,7}/(\Delta E_{6,7})$	$\Delta H_{6,8}/(\Delta E_{6,8})$	$\Delta H_{8,9}/(\Delta E_{8,9})$	$\Delta H_{8,10}/(\Delta E_{8,10})$
PM3	268.21	50.63	180.98	–8 9.14	191.91	2.72	175.74	–91.01
MINDO/3[8]	227.0	–1. 50	146.50	–14 7.0	156.5	–72 .0	104.0	–20 3.0
RHF/DZV-1d	350.78	80.44	349.95	-4 6.94	296.92	76.10	375.0	34.50
MP2/RHF/DZV-1d	316.35	88.24	274.00	-4 6.94	269.81	77.21	238.43	13.38
MP3	317.82	69.45	311.33	-3 4.14	–	–	–	–
MP4 (DQ)	318.23	72.17	307.19	39.50	–	–	–	–
CCD	319.41	71.79	306.85	-4 1.09	–	–	–	–

[a] $\Delta H_{i,j}$ are the reaction barriers calculated from the enthalpies of compounds by the PM3 method; $\Delta E_{i,j}$ are reaction barriers found from total energies by *ab initio* calculations.

geometrical parameters in the series of nitroalkanes.[14,15] However, according to *ab initio* calculations, the *R*(C–N) values in NM and DNM are virtually identical, the accumulation of nitro groups resulting in a substantial decrease in *R*(N–O). A similar decrease in *R*(N–O) (although less pronounced) is also indicated by PM3. The C–H and N–O bonds change most appreciably in the TS according to both *ab initio* and PM3 methods. At the same time, the changes in *R*(C–NO $_2$) are relatively small. In addition, the *ab initio* calculations predict the most pronounced elongation for the C–N O_2 bond, whereas PM3, conversely, points to its slight shortening. Thus, according to *ab initio* calculations, the geometrical parameters of the TS are closer to those of the aci-forms; therefore, in conformity with the Hammonds rule, the barrier for the reaction found from the *ab initio* results is markedly (60–80 kJ mol^{-1}) higher than that found by PM3. The C–H bond in the TS for the reaction of DNM is substantially shorter that in the reaction of NM; according to the Hammonds rule, this lowers considerably the energy barrier to the reaction. According to the *ab initio* and PM3 data, this lowering amounts to 46.5 and 76.3 kJ mol^{-1}, respectively.

The results listed in Table 2 indicate that the formation of the aci-form is the rate-determining step in reactions (1) and (2). The barrier to the second step elimination of water is markedly lower, its height depending only slightly on the number of nitro groups. In all cases, the allowance for electron correlation within the framework of the MP2 procedure substantially decreases the energy barriers in the reactions in question. Analysis of the *ab initio* results (Table 1) indicates that the N–O bond in the TS has almost completely cleaved, and the *R*(C–N) and *R*(C–H) distances differ insignificantly from the corresponding values found for the aci-forms. According to the PM3 data, in addition to the very significant increase in the *R*(N–O) v alue, the C–H bond in the TS is also substantially longer. Thus, the *ab initio* and PM3 calculations lead to somewhat different reaction mechanisms. Based on the *ab initio* results, one can believe that the elimination of water begins most likely with an intramolecular transfer of oxygen. However, the structure of the TS predicted by both the N–O and C–H bonds are markedly elongated. In general, changes in the valence bond lengths for the TS found by the *ab initio* method are larger than those predicted by PM3. The structure found by the latter is closer to the reaction products; therefore, the energy barrier calculated by this method is noticeably higher.

Thus, our study confirms the previous[8] conclusion that accumulation of nitro groups decreases appreciably the energy barrier to the formation of the aci-form. It is of interest that a similar tendency is also retained for trinitromethane (TNM). According to PM3 data, the barrier to the formation of the aci-form in TNM is 142.5 kJ mol^{-1}, which is more than 30 kJ mol^{-1} lower than the *D*(C–N) in this compoun d (173.9 kJ mol^{-1})[3] and is almost 50 kJ mol^{-1} lower than the barrier for DNM. Thus, the decrease in the barrier to the formation of the aci-form in the series NM, DNM, TNM is much more pronounced than the decrease in *D*(C–N) [by 125.5 kJ mol^{-1} (PM3) and 57–71 kJ mol^{-1} (from various experimental estimates[3]), respectively]. However, the magnitudes of the barriers for the reactions of NM and DNM are fairly large; therefore, the occurrence of these steps during unimolecular gas-phase decomposition appears relatively unlikely.

However, it should be borne in mind that the barriers to the isomerisation and unimolecular decomposition of aliphatic C-nitro compounds found by *ab initio* calculations are, apparently, somewhat overestimated. In fact, our study of the TS in the β-elimination of nitrous acid from nitroethane and 1-nitropropane (MP2/6-31 G*/3-21G)[16] has shown that the calculated activation enthalpies are almost 60 kJ mol^{-1} larger than experimental activation energies for the gas-phase decomposition. Therefore, it can be assumed that the barriers for the reactions of NM and DNM found by us are upper estimates. We believe that the results obtained by PM3 can be taken as lower limits for the variation of the barriers to the aci-forms. In fact, this method predicts fairly adequately (much better than MINDO/3) the enthalpies of formation of NM and DNM. The calculated enthalpies of formation (–66. 7 and –50. 0 kJ mol^{-1}) are quite close to the experimental values (–80. 7 and –59. 8 kJ mol^{-1}).[17] It can be seen from Table 2 that the enthalpies of formation of the NM aci-form predicted by the PM3 and *ab initio* also differ insignificantly. It is noteworthy that the verification of the influence of allowance for electron correlation has shown that the reaction barriers found by MP3 and MP4(DQ) procedures change only slightly (by less than 2 kJ mol^{-1}) and the MPx series converges well to the CCD values, whereas in the case of the enthalpy for the reaction of formation of the aci-form, the CCD procedure markedly decreases the corresponding values compared to those found by MP2. In this case, we found the ΔH_ρ value equal to 71.8 kJ mol^{-1}. Comparison with the result given in Table 2 indicates that this estimate is 16 kJ mol^{-1} closer to the PM3 data than the MP2 result.

Therefore, in our opinion, there are no grounds for ruling out completely the transformations related to the formation of the aci-forms in the gas-phase decomposition of trinitromethane even without high pressures. As regards the reactions involving NM and especially DNM, the processes studied in this and in the previous[8] papers, can evidently occur as well during the liquid-phase decomposition, because the corresponding barriers can decrease appreciably owing to specific solvation. This is indicated by the experimental detection of the aci-forms of mononitro- and dinitro-compounds.[1,3,5] Later, we intend to perform an appropriate investigation using the results obtained in the present study and methods that permit correct allowance for the influence of the medium and also to consider the effect of pressure on the volume and enthalpy of activation for the gas-phase decomposition of NM and DNM.

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