Ab Initio Studies of Triazenes in Relation to Experimental Findings

Ann Schmiedekamp,*,† Richard H. Smith, Jr.,‡ and Christopher J. Michejda*,‡

Department of Physics, Pennsylvania State University at Ogontz, Abington, Pennsylvania 19001, and Laboratory of Chemical and Physical Carcinogenesis, BRI-Basic Research Program, NCI-Frederick Cancer Research Facility, Frederick, Maryland 21701

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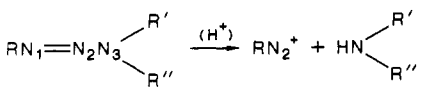
The sites of protonation of triazene ($HN{=}NNH_2$), 1-methyltriazene, and 1,3-dimethyltriazene were investigated by ab initio molecular orbital calculations. Proton affinities, $E(AH)^+ - E(A)$, were calculated for each possible geometry-optimized triazene species. The proton affinities for (*E*)-triazene were calculated at the 3-21G basis set level; then single-point calculations of the 3-21G geometries were carried out with the 6-31G* basis to test the effect of a larger basis set. Møller–Plesset perturbation theory to the third order was used to obtain the correlation correction. The Hartree–Fock level calculations were found to be in agreement with those which included correlation in predicting that the preferred site of protonation was N_1. Proton affinities of 1-methyltriazene and 1,3-dimethyltriazene (both cisoid and transoid), calculated at the 3-21G level, also predicted that N_1 was the preferred site of protonation. Kinetic studies on the acid-catalyzed decomposition of triazenes have suggested that protonation at N_3 is the key step which leads to heterolysis. The calculated proton affinities reveal that protonation at N_3, although slightly less favorable than protonation at N_1, results in a molecule in which the N_2–N_3 bond is considerably elongated. These theoretical findings suggest that although protonation at N_1 may be thermodynamically preferred, protonation at N_3 leads to a structure which is predisposed to heterolysis of the N_2–N_3 bond. Proton affinity calculations on (*Z*)-triazene showed that the preferred site of protonation was N_1 but that attempts to attach a proton to N_3 resulted in the scission of the N_2–N_3 bond. Possible mechanistic implications of that finding are discussed.

Introduction

Triazenes are compounds which are stable to aprotic media but readily undergo acid-catalyzed decomposition to diazonium ions and the corresponding amines.



Extensive kinetic studies of the decomposition of 1,3,3-trialkyltriazenes[1,2] and 1,3-dialkyltriazenes[3] have been carried out. The reactions are catalyzed by specific acid. The salient feature of the mechanism for both classes of triazenes is that the heterolysis occurs following protonation at N_3. The initial protonation is fast and reversible. In order to gain a better understanding of the protonation reaction, we carried out ab initio molecular orbital calculations on the protonation of triazene (R = R′ = R″ = H), methyltriazene (R = Me, R′ = R″ = H), and 1,3-dimethyltriazene (R = R′ = Me, R″ = H). During the course of this work Nguyen and Hoesch[4] reported their results, on, inter alia, protonation of (*E*)-triazene. Their calculations are in complete agreement with our studies. Our data, however, extend to the methylated homologues, which allow a direct comparison to be made with experimental results. This paper addresses the preferred sites of protonation (N_1, N_2, or N_3), the protonation of the (*Z*)-triazene and the effect of methyl substitution on relative proton affinities.

Methods

Ab initio molecular orbital calculations were performed by using the GAUSSIAN 82 program.[5] Geometry-optimized wave functions for triazene and its three protonated species (protonation at N_1, N_2, and N_3) were calculated at the 3-21G basis level. Proton affinities, defined as $E(AH)^+ - E(A)$, were determined. Similar calculations were performed for 1-methyltriazene and 1,3-dimethyltriazene, and the proton affinities for these compounds were determined. The effects of a larger basis set, as well as of correlation energy, were probed by single-point calculations of the 3-21G geometries of (*E*)-triazene using HF/6-31G* and the Møller–Plesset perturbation theory (MP2 and MP3), respectively. Basis set superposition errors[6] were determined for each proton affinity calculation and the tables of proton affinity values are corrected for this effect. The basis set superposition error results from the fact that calculations of the protonated and unprotonated triazenes involve a different number of basis functions, since the protonated triazenes require additional functions for the extra hydrogen. In order to correct for the problem, the calculations on the unprotonated triazenes were carried out with a dummy atom at the position of the additional proton at the geometry of the protonated species. This allows a

Table I. Proton Affinities (kcal/mol)

protonated on	3-21G	6-31G*[a]	MP2/6-31G*[a]	MP3/6-31G*[a]
		(*E*)-Triazene		
N_1	231.8	227.6	221.3	223.7
N_2	199.0	196.9	198.7	199.2
N_3	222.2	218.8	215.1	216.4
		1-Methyltriazene (**3**)		
N_1	237.5			
N_2	210.5			
N_3	233.5			
		Cisoid 1,3-Dimethyltriazene (**4**)		
N_1	244.4			
N_3	240.3[b]			
	242.4[c]			
		Transoid 1,3-Dimethyltriazene (**5**)		
N_1	244.9			
N_3	235.7			

[a] Single-point calculation at 3-21G-optimized geometry. [b] Calculated for structure **4b**. [c] Calculated for structure **4b′**.

† Pennsylvania State University at Ogontz.
‡ NCI-Frederick Cancer Research Facility.

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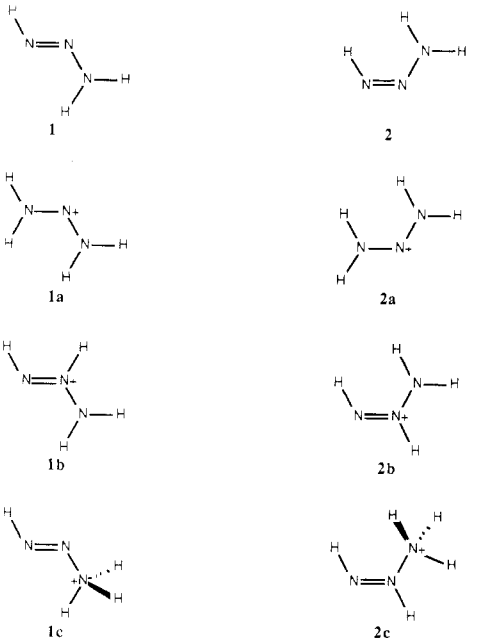

Figure 1. Structures of the neutral and protonated *E* and *Z* isomers of triazene used in the computation of energies and proton affinities at the 3-21G, 6-31G*, MP2/6-31G*, and MP3/6-31G* levels.

Table II. Total Energies Calculated for Neutral and Protonated Triazene, 1-Methyltriazene, and 1,3-Dimethyltriazene

	energy (hartrees)		
structure	3-21G	6-31G*	MP3/6-31G*
1	−164.06462	−165.00879	−165.50913
1a	−164.42856	−165.36204	−165.85730
1b	−164.38000	−165.31735	−165.82038
1c	−164.40630	−165.33565	−165.83781
2	−164.-5444		
2a	−164.42856		
2b	−164.37834		
2c	no equilibrium structure		
3	−202.88229		
3a	−203.25514		
3b	−203.21508		
3c	−203.23853		
4	−241.69754		
4a	−242.07974		
4b	−242.06251		
4b′	−242.06620		
5	−241.69543		
5a	−242.07836		
5b	−242.06415		
6	−241.67813		
7	−241.66744		

calculation with the same number of basis functions, thereby correcting for the slight energy difference produced by exclusion of the hydrogen basis functions.

Results

Table I shows the proton affinities of (*E*)-triazene, (*E*)-1-methyltriazene, and the cisoid and transoid rotamers of (*E*)-1,3-dimethyltriazene calculated from the optimized wave functions at the 3-21G basis level. The values in Table I were calculated from the difference between the total energy of the protonated forms and the corresponding neutrals. The total energies for the structures shown in Figures 1 and 2 are listed in Table II. In accord with the results of Nguyen and Hoesch,[4] the N_1 nitrogen of triazene had the highest proton affinity, with N_3 being a close second. Our results differ slightly from theirs because we

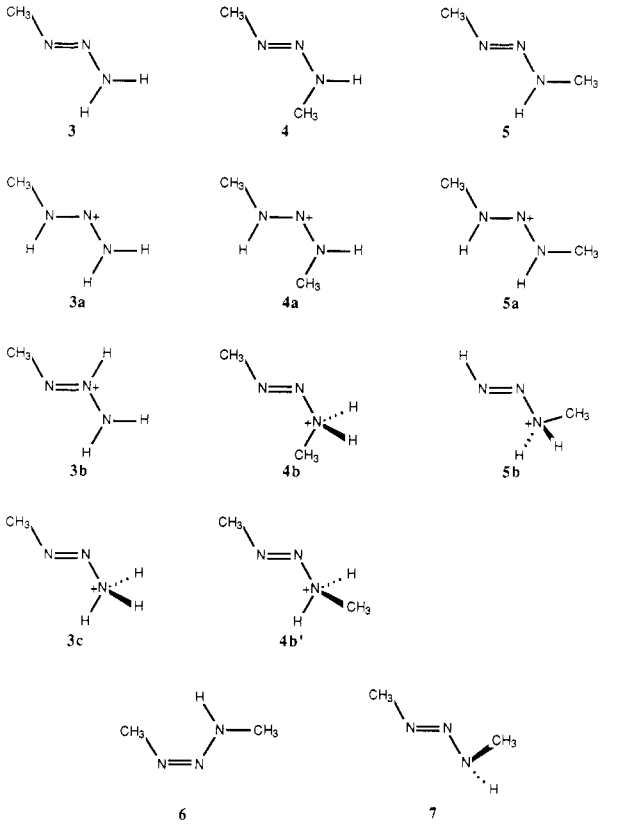

Figure 2. Structures of methylated triazenes used in the calculations of total energies and proton affinities. These structures were optimized at the 3-21G level.

have included a correction for basis set superposition error (see Methods). Interestingly the substitution of methyls on N_1 and N_3 did not change the order; apparently methyl substitution did not introduce enough asymmetry to change the energetically preferred protonation site. The differences in proton affinity values at N_1 and at N_3 are small.

Table I also shows the results of more stringent single-point calculations of (*E*)-triazene at the 3-21G-optimized geometry. The proton affinities were calculated by Hartree–Fock SCF method at the 6-31G* basis level and calculations of correlation energy were also made. The use of the polarized basis set and the inclusion of MP2 and MP3 decreased the proton affinities. Similar basis set effects on proton affinities were observed by Nguyen and Hoesch.[4] The diferences in proton affinities between N_1 and N_3, and between N_1 and N_2, are consistent as one goes from 3-21G all the way to MP3/6-31G*. In an earlier publication Nguyen et al.[7] found that the geometries optimized at the 3-21G and 3-31G basis level were close. These workers also calculated the energy difference between the (*E*)- and (*Z*)-triazene at the 3-21G and 6-31G basis levels. In the subsequent paper,[4] additional calculations at the 6-31G*, 6-31G**, and MP2/6-31G** level were presented. The energy differences between the *E* and *Z* structures were relatively small and not very sensitive to basis set changes. The *E* isomer had a slightly lower energy than the *Z*, with difference in magnitude being on the order of 23–30 kJ/mol (5.5–7.2 kcal/mol). The change in the difference in energy between the *E* and *Z* isomers calculated at the 3-21G basis and the 6-31G* basis was found to be 0.8 kcal/mol. The consistency of our results

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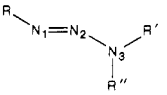
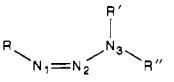
Table III. Structural Parameters for Triazenes and Their Protonated Forms Derived from the Optimized Geometries[a] Computed in the 3-21G Basis

	structural parameters						
	bond lengths (Å)			bond angles (deg)			
compd	R–N_1	N_1–N_2	N_2–N_3	<RN_1N_2	<$N_1N_2N_3$	<$R''N_3N_2$	<$R'N_3N_2$
1	1.018	1.243	1.360	108.2	113.6	118.9	116.9
1a	1.004	1.272	1.272	115.9	120.4	123.9	115.9
1b	1.018	1.223	1.348	114.1	121.0	116.2	118.7
1c	1.023	1.202	1.582	112.1	107.3	109.7	106.9
2	1.029	1.235	1.375	113.9	119.1	121.5	116.2
2a	1.004	1.272	1.272	123.9	120.4	123.9	115.9
2b	1.021	1.222	1.356	115.2	128.9	119.1	117.6
3	1.478	1.237	1.370	113.2	113.7	119.1	116.6
3a	1.493	1.261	1.285	119.3	120.5	123.7	115.8
3b	1.487	1.218	1.364	118.9	121.6	116.1	118.2
3c	1.509	1.194	1.627	116.5	107.4	109.2	105.6
4	1.477	1.240	1.364	113.0	114.3	122.1	114.2
4a	1.489	1.269	1.280	118.9	120.6	126.2	113.1
4b	1.511	1.197	1.593	116.1	109.2	116.2	103.7
4b′	1.498	1.207	1.557	115.9	108.1	108.2	105.8
5	1.478	1.239	1.365	113.1	114.1	117.4	117.8
5a	1.489	1.272	1.274	119.2	120.8	121.1	118.5
5b	1.500	1.204	1.578	115.9	108.3	107.7	107.3

[a] Calculations were carried out on structures restricted to C_s geometry. [b] Numbers for structures refer to those in the figures. [c] Parameters derived from the following structures:





and the calculations of Nguyen and Hoesch[4] suggested that the 3-21G basis set was adequate for the triazene systems considered. Thus, all the calculations on the methyltriazenes were carried out only at the 3-21G level as a result of confidence in this basis. It should also be pointed out that protonation of the *E* isomer of triazene resulted in considerable elongation of the N_2–N_3 bond, from 1.36 Å in triazene to 1.58 Å in the N_3-protonated form. A similar bond elongation was found by Nguyen and Hoesch.[4]

Protonation of the *Z* isomer of triazene was also investigated at the 3-21G basis level. Protonation at N_1 (proton affinity = 231.8 kcal/mol) was preferred over N_2 by more than 30 kcal/mol. Protonation of N_3 in (*Z*)-triazene, however, did not yield a stable structure; the molecule split along the N_2–N_3 bond.

Several configurations of 1,3-dimethyltriazene were calculated at the 3-21G basis level. The most stable configuration was *E*-cisoid, **4**. However, the *E*-transoid **5** was only 1.5 kcal/mol higher in energy. The *Z*-transoid **6** was 12.2 kcal/mol higher than *E*-cisoid and an intermediate form **7**, where the methyl and the hydrogen on N_3 are perpendicular to the plane defined by N_1, N_2, and N_3 was 18.9 kcal/mol higher than *E*-cisoid. The proton affinities were calculated for structures **4** and **5** (Table I).

Discussion

The calculations on triazene presented in this paper, and those already reported by Nguyen and Hoesch,[4] define most of the parameters needed to understand how triazenes should behave when exposed to acid. The calculations on the methylated triazenes indicate that these compounds behave qualitatively in a manner similar to the parent compound. The calculations show clearly that the preferred site of protonation for all of the triazenes studied is N_1. It might be argued that in view of the small energy difference in protonation at N_1 versus N_3, the order of protonation may be changed by inclusion of a zero-point energy correction and/or geometry optimization at a basis level higher than 3-21G. While our geometry optimizations were carried out only on the 3-21G level, the earlier calculations of Nguyen et al.[4,7] suggested that 3-21G were not markedly improved by higher level bases. Nevertheless, this argument cannot be discounted completely on the basis of the present data, particularly because no zero-point energy correction was calculated. However, N_1 would also have been predicted intuitively to be most stable since that protonated structure would allow for the greatest delocalization of charge over the three nitrogen atoms. Protonation at N_1, however, does not appear to be a realistic intermediate for the subsequent dissociation of the triazene. Our kinetic data[1-3] argue for protonation at N_3 as the critical step which leads to heterolysis of the N_2–N_3 bond. The calculations indicate that protonation at N_3 is only a few kilocalories less favorable than protonation at N_1. Moreover, protonation at N_3 leads to a considerable bond-lengthening of the N_2–N_3 bond (1.360 to 1.582 Å). The lengthening of the bond which is broken in the subsequent step can be viewed as the predisposing factor which results in heterolysis. The N_3-protonated triazene is well on its way to becoming a diazonium ion in tight association with the corresponding amine. It is interesting to note that the lengthening of the N_2–N_3 bond following protonation in triazene is accompanied by a shortening of the N_1–N_2 bond (1.243 to 1.202 Å), as might be expected for a structure with partial triple bond between N_1 and N_2. The 3-21G-optimized geometries for the triazenes in Figures 1 and 2 are presented in Table III. It is apparent from these data that protonation of N_3 in all of the triazenes examined results in a considerable lengthening of the N_2–N_3 bond.

We also studied the protonation of the *Z* isomer of triazene (2). Interestingly, protonation at N_3 led to a synchronous breakage of the N_2–N_3 bond, i.e. the N_3-protonated form of 2 was not stable. Sutherland[8] studied the decomposition of triazene formed by radiolysis of hydrazine sulfate in aqueous solution. His data indicated

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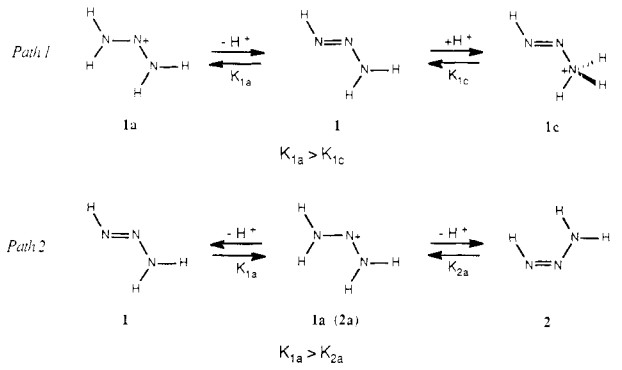
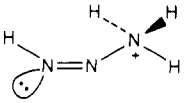
Scheme I



that the pseudo-first-order rate constants of the reaction had complex pH profile. The triazene decomposed in a pH-independent fashion at low pH (0.8–4.0). At higher pH, the rate constant decreased linearly (slope −1.0) with increasing pH to a sharp minimum at pH ~9.0, whereupon the rate constants increased linearly (slope 1.0) to another pH-independent region (pH 11.5–12.5) and then decreased again at higher pH. The data permitted the determination of pK_a of 5.0 for the protonated triazene. Based on the present calculations, it can be assumed that the dominant protonated form is 1a. It is not obvious how this species could decay to products with the observed rate constant of 133 s^{-1}. Direct transfer of a proton from N_1 to N_3 is not favorable because of orbital symmetry considerations. However, two possible pathways exist, as shown in Scheme I.

Path 1 implies simply that the thermodynamically more favored form (1a) is in equilibrium with a form that leads to reaction (1c). This is a reasonable pathway and suffices to account for most data. Path 2, however, is intriguing. The symmetrical N_1-protonated triazene 1a can lose either a *Z* or an *E* proton from the terminal nitrogens. The loss of the *E* proton regenerates the (*E*)-triazene but the loss of the *Z* proton produces the (*Z*)-triazene. Thus, N_1 protonation can provide a route for *E* to *Z* isomerization. Subsequent protonation of the (*Z*)-triazene on N_3 could result in synchronous breakage of the N_2–N_3 bond. It is impossible to distinguish between the two pathways on the basis of the present data. Nguyen and Hoesch[4] calculated the energy difference between the (*E*)- and (*Z*)-triazene to be 22.9 kJ/mol (5.5 kcal/mol), at the MP2/6-31G** level. No experimental data are available on the energy barrier between the *E* and *Z* forms although it would be expected to be substantial since it would involve rotation of the N_1–N_2 double bond. Calculations of the configuration in which the H_1 proton was rotated 90° with respect to the HN_3H plane indicated that the barrier is at least 46.7 kcal/mol at the 3-21G level. Thus, protonation at N_1 provides a low energy route for the isomerization. The populations of the *Z* and *E* forms would then be governed by the enthalpy difference between them (~5–6 kcal/mol). The instability of the *Z* form protonated on N_3 is seen as a result of the antiperiplanar arrangement of the nonbonding electron pair on N_1 with the breaking N_2–N_3 bond, as shown in the following diagram.



Although there are no experimental data that would indicate the involvement of the *Z* form in the decomposition of 1,3-dialkyltriazenes, the studies of Sinnott and co-workers[9] on the decomposition alkylaryltriazenes in aqueous media may be interpreted in that fashion. These workers argued that the kinetics of proton-catalyzed decomposition of various alkylaryltriazenes were best accounted for if proton transfer to the aniline nitrogen occured synchronously with the breakage of the N–N bond, leading to the formation of the aniline and the alkyldiazonium ion. In view of the present computational results, it could be postulated that in their case there was a rapid acid-catalyed *E* to *Z* isomerization of the triazenes via the N_1-protonated species, followed by the rate-determining acid-induced fragmentation of the *Z* isomer. It is interesting to note that their kinetics appeared to involve proton transfer from a general acid, in contrast to our studies on dialkyl- and trialkyltriazenes which indicated specific acid catalysis.

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