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Quantum-chemical study of the singlet potential energy surface of the nitrene—dioxygen system

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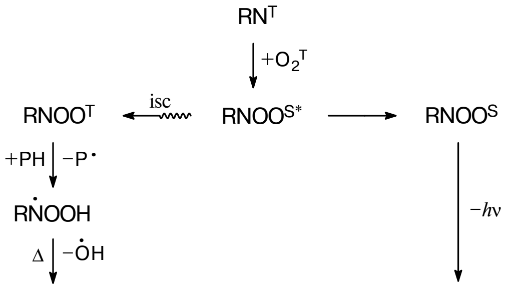
The potential energy surfaces of the HN—O_2 and PhN—O_2 systems were calculated by the MP2 and B3LYP methods. The mechanism of photooxidation of azides was refined. Photooxidation produces the nitrene—O_2 adducts with dioxaziridine and non-cyclic structures. The parameters of IR spectra of the adducts were calculated. The rearrangement of dioxaziridine to a nitro compound is likely a reason for chemiluminescence accompanying the photooxidation of azides.

Key words: photooxidation, dioxaziridine, azides, adducts, *ab initio* quantum-chemical calculations.

The mechanism of photooxidation (PO) of organic azides has been studied in several works.[1—5] However, the generally accepted scheme of this process is not available so far. The key intermediate of this reaction is an adduct of nitrene with O_2,[5] which further reacts according to Scheme 1 (symbols "S" and "T" designate the singlet and triplet states, respectively)[5,6]. The $RNOO^{S*}$ adduct in the excited singlet state formed by the interaction of the triplet nitrene and molecular oxygen can either non-radiatively be transformed into the triplet state or be rearranged to a nitro compound. Interest in the latter process increased because chemiluminescence accompanying PO of organic azides[7] has recently been observed, and this phenomenon can be induced only by excited singlet species.

Scheme 1



isc is intersystem crossing

Since experimental data on the properties of the nitrene—O_2 adducts are rather scanty, in this work we studied them by quantum-chemical methods.

Procedure of quantum-chemical calculations

The potential energy surface (PES) of the HN—O_2 system was calculated in the framework of the density functional theory (DFT)[8—10] with the B3LYP gradient hybrid functional[11] in the 6-31G(d) basis set. The PES cross sections were plotted by the "relaxed scan" method through partial optimization of the geometry of the molecule. One or several geometric parameters were taken constant, and the other parameters were optimized. Vibrational frequencies were calculated for all found stationary points.

The initial geometric parameters of the NO_2 fragment of the PhN—O_2 system during search for stationary points on the PES corresponded to the optimized parameters of the NO_2 fragment of the HN—O_2 system. The geometric parameters of the PhN—O_2 system were optimized by the MP2/6-31G(d), MP2/6-311G(d)[11—15], B3LYP/6-31G(d), and B3LYP/6-311G(d) methods. Vibrational frequencies for all stationary points on the PES were calculated by the B3LYP and MP2 methods.

The calculations were performed using the PC GAMESS program[16,17] and the GAUSSIAN 94 calculational complex[18] at the Supercomputer Center for Collective Use of the Russian Foundation for Basic Research in the Institute of Organic Chemistry of the Russian Academy of Sciences.

Results and Discussion

HN—O_2 system. The PES of HN—O_2 has several local minima corresponding to the adducts with O_2. Some of them have previously been studied by quantum-chemical methods. The results obtained are presented in Table 1. They allow us to conclude that the B3LYP/6-31G(d) and B3LYP/6-311G(3df,3pd) methods reproduce rather well results of more rigid and exact methods, for example, CCSD(T)/6-31G(d,p). The latter made it possible to use the B3LYP methods for

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Table 1. Results of quantum-chemical calculations of the PES of the HN—O_2 system and experimental geometric parameters for HONO

Adduct	Method of determination	Distance/nm				Angle H—N—O /deg	Ref.
		N—H	N—O	O—O′	HO—N		
HNO_2	B3LYP/6-31G	0.1044	0.1222	—	—	115.7	19
	B3LYP/6-311G(3df,3pd)	0.1042	0.1212	—	—	115.7	20
	B3LYP/6-311++G(d,p)	0.1044	0.1222	—	—	115.8*	21
	CCSD(T)/6-31G(d,p)	0.1035	0.1234	—	—	115.9**	21
HNOO	B3LYP/6-31G	0.1036	0.1431	0.1461	—	102.8	19
	B3LYP/6-311++G(d,p)	0.1036	0.1432	0.1460	—	—	21
	CCSD(T)/6-31G(d,p)	0.1033	0.1449	0.1491	—	—	21
HONO	B3LYP/6-31G	—	0.1179	—	0.1426	102.4	20
	B3LYP/6-311G(3df,3pd)	—	0.1163	—	0.1430	102.5	20
	B3LYP/6-311G(3df,3pd)	—	0.1171	—	0.1508	100.8	20
	SVWN/6-311G(3df,3pd)	—	0.1164	—	0.1416	101.7	20
	B3LYP/6-311++G(d,p)	—	0.1179	—	0.1427	102.3	21
	CCSD(T)/6-31G(d,p)	—	0.1192	—	0.1434	101.9	21
	Experiment	—	0.1177	—	0.1433	102.1	22

* A value of 122.1° has previously[21] been published, which is likely misprint.

** A presented value of 122.05° is likely misprint.

Table 2. Geometric parameters of stationary points on the PES of the HN—O_2 system calculated by the B3LYP/6-31G(d) method

Molecule	Distance/nm			Angle/deg		
	O—O	N—O	H—N	O—O—N	O—N—H	O—O—N—H
HNO_2*	0.2202	0.1222	0.1044	25.7	115.7	180.0
Z-HNOO**	0.1304	0.1266	0.1042	120.2	104.3	0.0
E-HNOO**	0.1289	0.1282	0.1034	117.3	100.1	180.0
H(NOO)***	0.1461	0.1431	0.1036	59.3	102.8	97.8

* Nitro compound.

** Non-cyclic nitrene—O_2 adduct.

*** Cyclic nitrene—O_2 adduct.

Table 3. Total energies (E_{tot}) of structures on the singlet PES of the RN—O_2 system

R	Calculation method	$-E_{tot}$/au			
		RNO_2	R(NOO)	*Z*-RNOO	*E*-RNOO
H	B3LYP/6-31G(d)	205.68694	205.56700	205.58031	205.57393
Ph	HF/6-31G(d)	434.17523	434.04992	434.04421	434.04575
	HF/6-311G(d)	434.26952	434.14300	434.13739	434.13885
	MP2/6-31G(d)	435.46841	435.34440	435.36345	435.36342
	MP2/6-311G(d)	435.65861	435.52861	435.55168	435.55012
	B3LYP/6-31G(d)	436.75059	436.62616	436.64317	436.64679
	B3LYP/6-311G(d)	436.85598	436.72594	436.74593	436.74936

plotting the PES of the HN—O_2 system and studying the energetics of rearrangements between the adducts with different geometric structures. The results of calculation are schematically presented in Fig. 1. The geometry and total energies of the adducts are given in Tables 2 and 3.

The formation of adducts from the initial triplet nitrene and O_2 molecule are energetically unfavorable. The non-cyclic adduct is capable of existing in two isomeric forms, *Z* and *E*. The energy of *Z*-HNOO is lower than that of *E*-HNOO by 4 kcal mol^{-1}.

The rearrangement of the non-cyclic nitrene—O_2 adduct to form the nitro compound occurs through the cyclic compound, *viz.*, dioxaziridine H(NOO).[2,19] The energy of dioxaziridine is by 8 kcal mol^{-1} higher than the energy of the non-cyclic adduct *Z*-HNOO. When

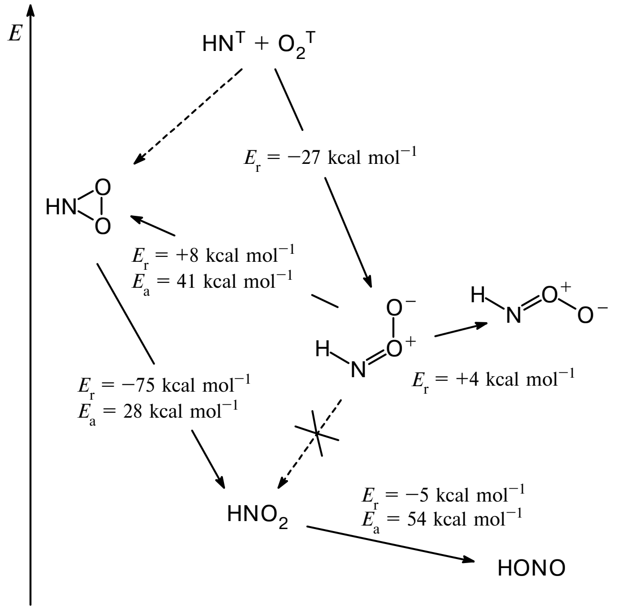


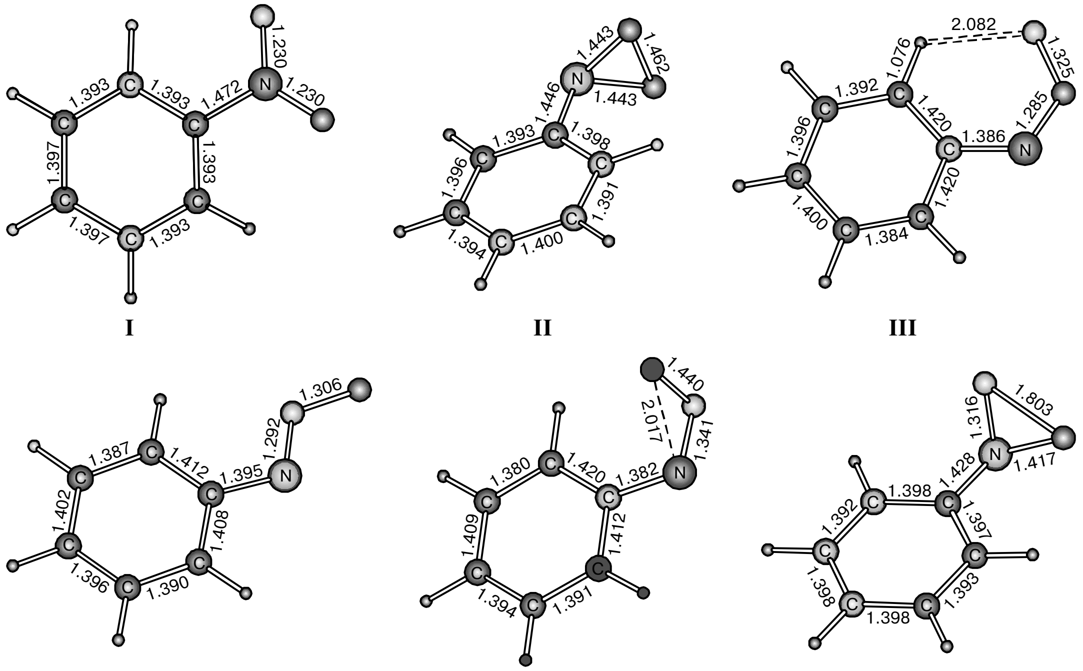
Fig. 1. Energy parameters for rearrangements of the nitrene HN—O_2 adducts calculated by the B3LYP/6-31G(d) method; E_r is the energy effect of the reaction, and E_a is its activation energy.

dioxaziridine is formed from the non-cyclic product, the N—O—O angle changes from 120 to 60°. The energy barrier to the reaction is 41 kcal mol^{-1}. Since the formation of a singlet species from two triplet species usually results in the vibrationally excited state,[23] this barrier can easily be surmounted, in particular, photochemically. At the same time, the reaction between nitrene and O_2 can immediately afford dioxaziridine.

The transition state was found for the rearrangement of the cyclic adduct into the nitro compound, and the energy barrier to the reaction is 28 kcal mol^{-1}. The reaction coordinate has such a value that the N—O and O—O bond lengths change simultaneously with the N—O—O angle opening. The rearrangement is an exothermic process, its energy effect being 75 kcal mol^{-1}.

One more minimum corresponding to the HONO molecule is present on the PES. Formation of the molecule of nitrous acid is more favorable than the formation of the molecule of nitro compound by 5 kcal mol^{-1}. The energy barrier to the rearrangement of nitro compound into HONO is 54 kcal mol^{-1}. In photochemistry this rearrangement is known as the nitro-nitrite rearrangement.[24]

PhN—O_2 system. Six stationary points corresponding to structures **I**—**VI** were found on the PES (Fig. 2). Nitrobenzene (see Fig. 2, structure **I**) and phenyldioxaziridine (see Fig. 2, structure **II**) have previously[19] been characterized by the B3LYP/6-31G(d) method. The results of studying the molecular geometry in crystal by X-ray diffraction analysis at −30 °C are also known[25] for nitrobenzene. The earlier calculated and experimental geometric parameters of the CNO_2 fragment in nitrobenzene and phenyldioxaziridine are presented in Table 4. Figure 3 schematically presents the results of calculation of the geometric structure and energy of the rearrangements for the stationary points



I **II** **III**

IV **V** **VI**

Fig. 2. Stationary points on the PES of the PhN—O_2 system (optimization by the B3LYP/6-31G(d) method); interatomic distances are presented in Å.

Table 4. Calculated by the B3LYP/6-31G method and experimental (in parentheses) geometric parameters of the CNO$_2$ fragment of structures **I** and **II**

Molecule	Distance/nm		Angle/deg		Ref.
	C—N	N—O	C—N—O	O—N—O′	
PhNO$_2$ (**I**)	0.1473	0.1230	117.7	121.15	19
	(0.1486)	(0.1208)	(118.0)	(121.0)	25
PhNOO (**II**)	0.1447	0.1443	124.3	60.9	19

Table 5. Difference of energies (ΔE)* of minima on the PES of the PhN—O$_2$ system

Calculation method	ΔE_1	ΔE_2	ΔE_3
	kcal mol^{-1}		
RHF/6-31G(d)	78.6	82.2	81.3
RHF/6-311G(d)	79.4	82.9	82.0
MP2/6-31G(d)	77.8	65.9	65.9
MP2/6-311G(d)	81.6	67.1	68.1
B3LYP/6-31G(d)	78.1	67.4	65.1
B3LYP/6-311G(d)	81.6	69.1	66.9

* The values of the difference in energies of the cyclic nitrene—O$_2$ adduct (phenyldioxaziridine) and nitrobenzene (ΔE_1), *Z*-tautomer of the non-cyclic adduct of nitrene with O$_2$ and nitrobenzene (ΔE_2), and *E*-tautomer of the non-cyclic adduct of nitrene with O$_2$ and nitrobenzene (ΔE_3) are presented.

on the PES of PhN—O$_2$. The total and relative energies of all calculated structures are presented in Tables 3 and 5, respectively.

The global minimum on the PES of the PhN—O$_2$ system corresponds to the nitrobenzene molecule (see Fig. 2, structure **I**). The cyclic nitrene—O$_2$ adduct, *viz.*, phenyldioxaziridine, lies by 78—82 kcal mol^{-1} higher by energy (see Fig. 2, structure **II**). All methods used reproduce this value (see Table 3), which confirms its reliability. The adduct is non-planar with a possible rotation about the C—N bond with an activation energy of 3.5 kcal mol^{-1}. The rotation about the C—N bond favors the easier achievement of the transition state of the rearrangement of phenyldioxaziridine into nitrobenzene (see Fig. 2, structure **VI**). The energy barrier of this process is 27 kcal mol^{-1}. A considerable energy effect of the reaction results in the situation where the nitro compound can be formed in the singlet excited state. Its transition to the ground state leads to the emission of a luminescence quantum in the visible spectral region. Chemiluminescence accompanying PO of azides was observed experimentally.[7]

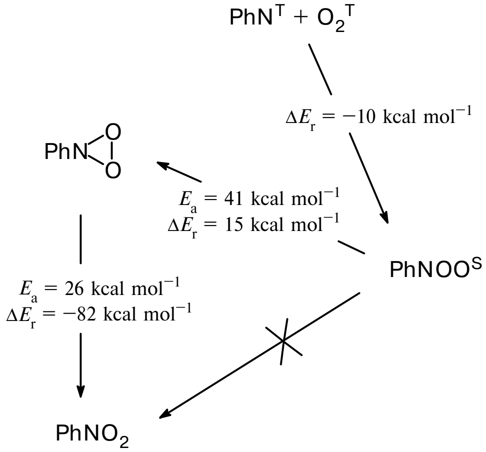


Fig. 3. Energy parameters for rearrangements of the phenylnitrene—O$_2$ adducts calculated by the B3LYP/6-31G(d) method; E_r is the energy effect of the reaction, and E_a is its activation energy.

The PES of the PhN—O$_2$ system has two minima corresponding to the *Z*- and *E*-tautomeric forms of the non-cyclic nitrene—O$_2$ adduct (see Fig. 2, structures **III** and **IV**). The difference in energies of these forms is 1—2 kcal mol^{-1}. The non-cyclic adducts are planar. According to published data,[4] the tautomeric structures of the adduct really exist at 77 K, and completely reversible photochromic transitions are possible between them.

The energy changes for rearrangement of the cyclic to non-cyclic adduct calculated ignoring and taking into account the electron correlation are different. In the first case, results indicate an insignificant preference of the cyclic structure. Taking into account the correlation, the non-cyclic structure is more stable than the cyclic one by 12—15 kcal mol^{-1}.

The activation energy corresponding to the transition state of rearrangement of the cyclic adduct into the non-cyclic *Z*-form (see Fig. 2, structure **V**) is 28 kcal mol^{-1}, which is only by 1 kcal mol^{-1} higher than that for the rearrangement of the cyclic adduct into nitrobenzene. The significant energy barriers (27 and 28 kcal mol^{-1}) for two possible routes of phenyldioxaziridine rearrangement indicate a sufficient kinetic stability of the dioxaziridine structure. The latter indicates a possibility of experimental detection of the dioxaziridine structure, for example, in low-temperature matrices.[19]

The results obtained unambiguously conclude that transition from the nitrene—O$_2$ adducts to nitrobenzene is exothermic process, and the energy evolved is quite sufficient for the emission of a chemiluminescence quantum. The rearrangement of the non-cyclic nitrene—O$_2$ adduct to the nitro compound occurs through the stage of formation of the cyclic adduct, *viz.*, dioxaziridine. The calculated frequencies and intensities of normal vibrations of the adducts of phenylnitrene with dioxygen are presented in Table 6. Available data on the calculation of the IR spectrum of nitrobenzene[26] show that the density functional method with the B3LYP functional in the 6-31G(d) basis set reproduces well experimental values of harmonic vibrations in the gas phase. Thus, calculated IR spectra of the nitrene—oxygen adducts can serve for the identification of adducts in experimental works.

Table 6. IR spectra of the phenylnitrene—O_2 adducts calculated by the B3LYP/6-31G(d) method

ν*/cm^{-1}	*I***/km mol^{-1}	ν*/cm^{-1}	*I***/km mol^{-1}	ν*/cm^{-1}	*I***/km mol^{-1}	ν*/cm^{-1}	*I***/km mol^{-1}
Z-PhNOO		*E*-PhNOO		Ph(NOO)		$PhNO_2$	
74	0.84	89	0.02	56	0.03	62	0.00
163	0.00	174	3.51	171	0.07	173	1.23
257	1.05	179	2.57	223	2.28	260	1.15
343	5.32	296	0.01	377	0.11	399	1.40
412	0.80	405	0.55	400	2.21	420	0.00
415	0.33	413	0.01	419	0.04	451	0.03
489	7.27	496	7.51	566	3.35	528	1.08
583	1.72	521	3.33	622	13.76	626	0.03
624	0.02	625	0.76	627	0.25	691	4.07
686	29.14	678	23.73	697	2.57	696	11.58
765	0.59	692	24.28	714	48.30	718	67.25
794	37.66	784	41.19	794	19.54	810	9.86
854	0.02	855	0.01	818	0.67	860	0.01
882	11.63	910	17.71	857	0.03	863	33.17
953	3.52	946	4.23	870	8.98	964	3.18
988	0.08	982	0.01	942	1.99	986	0.00
1008	4.59	1006	0.09	977	0.13	1012	0.27
1015	0.04	1012	1.59	1004	0.04	1021	0.30
1050	2.64	1049	0.41	1020	0.64	1050	3.77
1078	179.21	1113	16.01	1051	3.74	1109	7.23
1121	3.76	1180	208.02	1107	7.26	1131	31.50
1181	46.29	1194	2.87	1158	28.01	1195	0.24
1196	2.20	1197	59.98	1179	33.11	1206	2.88
1205	12.90	1213	5.78	1194	0.05	1346	0.71
1293	42.12	1276	10.27	1219	9.99	1375	11.39
1348	3.91	1364	0.30	1352	0.89	1400	280.45
1383	26.80	1376	3.10	1370	4.56	1504	0.67
1493	10.85	1505	9.66	1505	8.31	1528	7.91
1512	0.03	1528	1.98	1535	6.38	1626	153.82
1611	8.46	1630	1.08	1652	1.52	1648	4.16
1650	24.85	1648	13.81	1657	0.92	1677	58.65
3194	0.52	3196	0.25	3192	0.52	3197	0.84
3208	11.25	3206	10.87	3204	10.86	3209	13.29
3215	16.78	3216	17.34	3212	18.47	3219	14.71
3228	6.14	3228	6.30	3222	8.13	3253	1.18
3329	3.88	3237	2.35	3243	1.35	3253	1.84

* Wave number of normal vibrations.
** Intensity.

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