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Quantum Chemical Modeling of Photolysis of Hydrazine in the Presence of Triplet Nitromethane †

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Abstract

The study is devoted to the study of the photochemical interaction between triplet nitromethane and hydrazine in the singlet state. This work includes the application of modern methods of density functional theory (DFT) using various density functionals: B3LYP and ωB97XD, in combination with various basic sets. In the course of this study, it was possible to establish that this reaction proceeds by radical mechanism. The transition state (TS) is formed by the transfer of an oxygen atom from a triplet nitro compound to a singlet substrate along a linear trajectory with a relatively low activation energy. This study makes a contribution to understanding of mechanisms of TS formation and can be used in the development of new low-temperature methods for the oxidation of nitrogen-containing compounds.

Keywords: photochemistry; triplet state; nitro compound; DFT

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1. Introduction

Upon UV light absorption, nitromethane is able to transition from the ground S_0 state to the excited S_1, and then through the process of intersystem crossing conversion (*isc*) to the triplet T_1 state. Studies show that when decomposed by light, the results can vary greatly. The π(NO)–π*(NO) transition is observed in the energy range of 5.5–7 eV, and the σ(CN)–π*(NO) transition is observed in the 3.5–5 eV region [1]. Previous research using quantum chemical methods has focused on the most stable form of molecules [2]. When calculating of the formation energies using the DFT method and the B3LYP functional, the values can vary within 10 kcal/mol, depending on the selected basis. The best correspondence to experimental data is achieved using bases 6-31g(d) and 6-311g+(d,p). It is important to note that increasing of size of the basic set does not always improve the accuracy of calculations—after a certain limit, the quality of the results may deteriorate.

The study of the structure of hydrazine derivatives requires the use of modern analytical methods. The main research methods are NMR spectroscopy; UV spectroscopy; vibrational spectroscopy; photoelectron spectroscopy. Special attention is paid to the interaction of alone electron pairs which depends on the spatial arrangement of the MOs. Experimental data show that the hydrazine molecule has an asymmetric structure, which is confirmed by its dipole moment (1.83–1.90 Db) [3] and the results of spectroscopic studies. In our paper the mechanism of oxygen atom transfer from the nitro group of the triplet nitro compound to the nitrogen-containing substrate is considered. The main attention is paid to the formation of a TS during the interaction of reagents. For this purpose calculations are performed with various basic sets in order to determine the most appropriate method for such systems. The results obtained contribute to the development of new methods for processing organic compounds containing nitrogen.

2. Materials and Methods

To conduct the study, we used the Gaussian 09 quantum chemical complex [4], which allowed us to solve the following tasks: studying the reactivity of the compounds under study, modeling the structure of the transition state, determining the geometric and energy parameters of the system under consideration, and establishing the reaction mechanism. The Gaussian TS method was used to find the transition state. In the course of these quantum chemical calculations, the method of density functional theory (DFT) was used. The reliability of the results was confirmed by comparing our results with data from the literature on the corresponding reactions, also obtained by the DFT method, in particular with the oxidation of dimethyl sulfide by triplet nitro compounds [5]. In [5], the authors are of the opinion that this functionality is sufficient for calculating such systems.

3. Results

The reaction mechanism was studied using the example of the interaction of triplet nitromethane and hydrazine in the singlet state. These substances were selected as the simplest representatives of the corresponding classes. This reaction proceeds in two stages. At the first stage, nitromethane under the action of UV light passes from the ground state S_0 to the excited singlet state S_1 [6]. Next the $S_1 \rightarrow T_1$ transition is performed by intersystem crossing (*isc*). At the second stage, nitromethane in the triplet state interacts with hydrazine. The scheme of this reaction is shown in Figure 1.

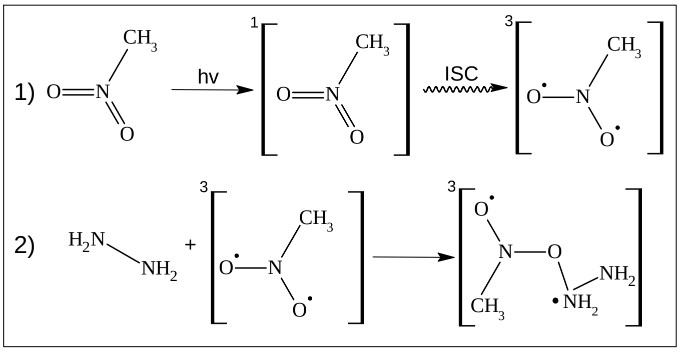

Figure 1. The mechanism of formation of the transition state.

The geometric structures of the compounds under consideration, as well as the transtion state formed during the study, are shown in Figure 2.

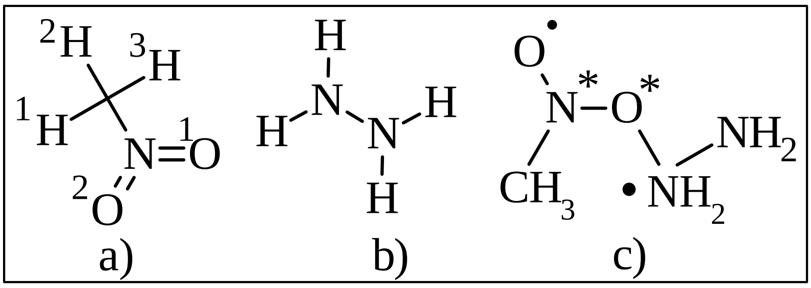

Figure 2. (**a**) Geometric structure of nitromethane; (**b**) Geometric structure of the guide; (**c**) Geometric structure of the transition state.

The calculated values obtained during quantum chemical calculations and the numerical data provided for verification are presented in Tables 1 and 2. The choice of the method for calculating the transition state was based on previous studies of nitromethane and hydrazine, also related to the quantum chemical calculation of the geometric structure [2,7,8].

Table 1. Geometric characteristics of nitromethane.

Method	Bond Length (Å)						Angles (deg.)		
	r C-N	r C-H^1	r C-H^2	r C-H^3	r N-O^1	r N-O^2	a CNO^1	a CNO^2	a ONO
B3LYP/6-31g	1.499	1.088	1.092	1.088	1.226	1.226	117.02	117.02	125.93
B3LYP/6-31g(d,p)	1.499	1.087	1.091	1.087	1.226	1.226	117.02	117.02	125.92
B3LYP/6-31g+(d,p)	1.500	1.088	1.091	1.088	1.228	1.228	117.22	117.23	125.51
B3LYP/6-311g+(d)	1.503	1.086	1.090	1.086	1.221	1.221	117.15	117.17	125.64
B3LYP/6-311g++(d,p)	1.503	1.086	1.090	1.086	1.221	1.221	117.15	117.15	125.64
CAM- B3LYP/6-311g++(3df,p)	1.487	1.082	1.086	1.082	1.210	1.210	117.19	117.21	125.56
ωB97XD/6-311g+(d,p)	1.492	1.086	1.089	1.086	1.212	1.212	117.20	117.22	125.54
Experiment *	1.489	1.089	1.089	1.089	1.224	1.224	117.35	117.35	125.3

Table 2. Geometric characteristics of hydrazine.

Method	Bond Length (Å)		Angles (deg.)	
	r(N-N)	r(N-H)	a HNH	a NNH
B3LYP/6-31g	1.488	1.023	102.20	103.12
B3LYP/6-31g(d,p)	1.489	1.022	102.12	103.24
B3LYP/6-31g+(d)	1.483	1.022	103.21	104.06
B3LYP/6-311g(d)	1.486	1.019	102.75	103.54
B3LYP/6-311g++(d,p)	1.431	1.016	108.62	112.85
CAM-B3LYP/6-31g(d)	1.473	1.020	102.61	103.67
ωB97XD/6-31g(d)	1.473	1.020	102.52	103.55
Experiment *	1.450	1.013	105.8	111.5
Experiment **	1.449	1.022	106	112

All calculations were performed using the DFT method. The lengths of C-N and N-O bonds and the angles of CNO and ONO were used as for nitromethane. In the case of hydrazine the N-N and N-H bonds attracted interest in the study and the HNH and NNH angles were also considered. According to Tables 1 and 2 the best results of the search for the excited state can be achieved using the B3LYP/6-311g++(d,p) method. Since the obtained geometric parameters of the considered initial components are most consistent with experimental data. The effectiveness of this calculation method for our system is due to the fact that the extended basic set provides the most accurate description of the electronic structure of molecules the B3LYP functional takes into account exchange and correlation effects and the preference for using diffuse functions is relevant since the system is considered in a triplet state. Table 3 shows the values of the atomic spin density distribution in the resulting intermediate. The results obtained confirm the presence of a biradical particle since the redistribution of spin density occurs heterogeneously between nitrogen and oxygen atoms which indicates the radical nature of this interaction.

Table 3. Distribution of the spin density in the transition state.

Method	Spin density			
	ϱ (N*)	ϱ (O*)	ϱ (N)	ϱ (O)
B3LYP/6-31g	0.8318	0.2280	0.1716	0.6588
B3LYP/6-31g(d)	0.7814	0.2467	0.1990	0.6433
B3LYP/6-31g+(d)	0.7931	0.1960	0.2282	0.6395
B3LYP/6-311g+(d)	0.7984	0.1994	0.2242	0.6481
B3LYP/6-311g++(d,p)	0.8068	0.1980	0.2079	0.6477
B3LYP/cc-pVDZ	0.7648	0.2338	0.1944	0.6596
B3LYP/cc-pVQZ	0.7730	0.1879	0.2253	0.6455
ωB97XD/6-31g(d)	0.8088	0.2134	0.2401	0.6265
ωB97XD/6-311g+(d,p)	0.8223	0.1623	0.2593	0.6357
ωB97XD/cc-pVQZ	0.7957	0.1586	0.2598	0.6293

The values of the energy barriers of the reaction are presented in Table 4. An analysis of the values obtained indicates that the B3LYP/6-311g++(d,p) method gives the most average results, in turn, the ωB97XD method for this system is less effective due to overestimated values.

Table 4. Activation energies of the reaction under study.

Method	$\Delta G^{\neq}$, kJ/mol
B3LYP/6-31g	256.4
B3LYP/6-31g+(d)	330.1
B3LYP/6-311g+(d)	329.7
B3LYP/6-311g++(d,p)	335.2
B3LYP/cc-pVDZ	340.2
B3LYP/cc-pVQZ	349.1
ωB97XD/6-31g(d)	425.2
ωB97XD/6-311g+(d,p)	361.9
ωB97XD/cc-pVQZ	378.5

4. Conclusions

A study of the reaction mechanism between hydrazine in the singlet state and in the triplet nitromethane showed the formation of a transition state in two stages. The result of the reaction is the formation of a biradical particle, a key intermediate product of this photochemical mechanism. To find the optimal quantum chemical set that can best describe the system, a comparative analysis of various methods and basic sets was carried out. As a result of quantum chemical calculations, it was found that the best results are achieved using the B3LYP/6-311g++(d,p) method, which provides an optimal balance between modeling accuracy and computational resources.

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