Photochemical Mechanism of the 1,3-Cycloaddition of Ethene to Benzene

Frank Neumann and Karl Jug*

Theoretische Chemie, Universität Hannover, Am Kleinen Felde 30, 30167 Hannover, Germany Received: March 16, 1994; In Final Form: August 23, 1994[®]

The mechanism of the photochemical 1,3-cycloaddition of ethene to benzene was investigated by the semiempirical MO method SINDO1. The relevant first excited singlet potential energy hypersurface was studied, and intermediates and transition structures were optimized with limited configuration interaction (CI). Two different reaction pathways proposed by experimentalists were compared. From the calculated barriers, a mechanism which involves a prefulvene structure is favored, whereas a simultaneous 1,3-cycloaddition via an exciplex mechanism seems most unlikely.

1. Introduction

It is well-known that benzene rearranges to benzvalene or fulvene¹ in small yield after excitation to the $S_1(B_{2\mu})$ state (254) nm, 4.9 eV). Attempts to trap the formed fulvene in situ with maleic acid anhydride failed, because a 1,2-photocycloaddition at benzene took place instead. The 1,3-photocycloaddition of alkenes to arenes was detected simultaneously by Wilzbach and Kaplan³ and Bryce-Smith et al.⁴ with alkenes without acceptor groups. The 1,3-photocycloaddition of alkenes to arenes is of great interest for natural product synthesis.^{2,5-8} Two different mechanisms are used as an explanation by experimentalists. The first mechanism is presented in Figure 1. This mechanism leads to a prefulvene structure. Here a bond is formed between $C^{(4)}$ and $C^{(6)}$. Subsequently, the product tricyclo[3.3.0.0^{4.6}]oct-2ene is formed by addition of the alkene. Alternatively, the formation of a bond between $C^{(1)}$ and $C^{(5)}$ can lead to benzvalene and the breaking of the bond $C^{(5)}-C^{(6)}$ with subsequent hydrogen shift from $C^{(4)}$ to $C^{(5)}$ to fulvene. The second mechanism involves an exciplex and is shown in Figure 2 for the addition of benzene and ethene. A change of substituents at benzene or alkene causes great changes in the experiments. In the vapor phase, fluorescence quenching of benzene barely takes place by addition of alkenes. Also, strong suppression of the formation of fulvene or benzvalene, respectively, is observed. Therefore, a prefulvene mechanism⁹ is very likely. But most experiments are done in solution where the exciplex mechanism is accepted by experimentalists.¹⁰ To resolve the mechanism, substituted benzenes were used in the experiments. For the prefulvene structure as well as for the intermediate in Figure 2, an alkyl substituent can be bound at center 1,3 or 5 due to its radical-stabilizing effect. This leads to differently substituted tricycles (Figure 1 and Figure 2) in further reaction to the product. In experiments, both mechanisms were found to be dependent on the substituents and used alkenes.⁹ Since the steric arrangement of the alkene is conserved during the reaction, the experimentalists concluded that the formation of the bonds $C^{(1)}-C^{(14)}$ and $C^{(5)}-C^{(13)}$ (Figure 1) occurs simultaneously or at least quasi-simultaneously.9 This suggests an exciplex mechanism.

2. Methods of Calculation

The calculations were performed with the semiempirical molecular orbital (MO) method SINDO1 with an extension to second- and third-row elements.¹¹ The suitability of SINDO1



Figure 1. Proposed experimental reaction scheme for the prefulvene mechanism.



Figure 2. Proposed experimental reaction scheme for the exciplex mechanism.

for photochemical reaction studies was demonstrated repeatedly.¹²⁻¹⁹ In the following, we denote the ground state by R_0 , the vertically excited singlet states by R_1 , R_2 , etc., and the singlet state curves by S_0 , S_1 , etc. The intermediates on the singlet surfaces are denoted by I_{1b} and I_{0a} . Minima including intermediates are characterized by exclusively positive roots of the force constant matrix, whereas transition structures have one negative root. Ground and excited equilibrium structures were optimized by a Newton-Raphson procedure. Bond lengths were optimized within 1% and bond angles and dihedral angles within 1°. Excited-state structures were optimized on their respective configuration interaction (CI) surfaces. Further details of the optimization procedure can be found in the furan treatment.¹² Single excitations are sufficient to get good agreement with the experimental vertical spectra. Double excitations are included for the avoided crossings along the reaction pathway. Triple excitations are beyond the present scope of SINDO1. The size of configuration interaction was adjusted to guarantee an unambiguous qualitative explanation of the mechanism. Thus, all energies and properties of the optimized structures of the system benzene-ethene were calculated with a 479 \times 479 CI which includes all single excitations from the 11 highest occupied MOs (OMOs) to all 21 unoccupied MOs (UMOs) plus double excitations from next-HOMO/HOMO to LUMO/next-LUMO. The vertical excitation spectrum of benzene was calculated with a 279 \times 279 CI which results from the system benzene-ethene taking into account only those excitations which are localized in the benzene system.

3. Results and Discussion

3.1. Exciplex Mechanism. The 1,3-photocycloaddition starts by an excitation to the $S_1(B_{2u})$ state.¹ The transition is symmetry forbidden but can occur by vibronic coupling. Figure 3 shows the 1,3-addition of ethene to benzene via the exciplex

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Figure 3. Reaction scheme for the exciplex mechanism.



Figure 4. Potential curves for the 1,3-photocycloaddition of ethene to benzene via exciplex formation, optimized points of geometry in circles (\bigcirc) .

TABLE 1: Bond Lengths (r, Å) and Angles $(\alpha, \text{ deg})$ of Reactant, Intermediates, and Product of the Photocycloaddition of Ethene to Benzene

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state	$R_0(D_{6h})$	$I_{0a}(C_s)$	I_{1b}	\mathbf{P}_0^a	$\mathbf{P}_0{}^b$
<i>r</i> ₁₂	1.423	1.413	1.417	1.553	1.575
r ₁₅	2.465	2.388	2.573	1.545	2.518
r_{16}	1.423	1.548	1.495	1.568	1.626
<i>r</i> 114		2.665		3.655	1.599
<i>r</i> ₂₃	1.423	1.413	1.424	1.356	1.356
r ₃₄	1.423	1.548	1.485	1.575	1.553
r ₄₅	1.423	1.526	1.512	1.626	1.568
r 46	2.465	2.432	1.645	2.518	1.545
r ₄₁₃		1.596		1.599	3.655
r ₅₆	1.423	1.526	1.471	1.531	1.531
r513		2.405		2.528	1.576
r ₆₁₄		1.596		1.576	2.528
<i>r</i> ₁₃₁₄	1.323	1.575	1.323	1.582	1.582
α123	120.0	119.8	109.3	110.7	111.9
a165	120.0	101.9	120.3	59.8	105.8
α_{216}	120.0	119.3	112.7	123.7	102.1
α ₂₁₁₄		81.3		96.1	110.0
α ₂₃₄	120.0	119.3	111.9	111.9	110.7
a ₃₄₅	120.0	101.9	120.7	102.1	123.7
α ₃₄₁₃		115.9		110.0	96.1
α456	120.0	105.7	66.9	105.8	59.8
α_{5614}		100.8		109.2	72.3
α6513		40.7		72.3	109.2

^a Numbering as in figures. ^b Numbering as in figures.

mechanism, Figure 4 the corresponding potential energy behavior in the $S_1(A'')$ state. The double excitations, which are important for the description of the intermediate, lower the ground state of benzene by 1.12 eV. This leads to a strong shift of the spectrum (Figure 3) and a relatively high deviation from the experimental spectrum.

The geometries of the stationary points involved in the reactions are contained in Tables 1 and 2. The reaction coordinates in Figure 4 are the distances $r_{4,13}$ and $r_{6,14}$. C_s symmetry was maintained during the reaction. Therefore, $r_{4,13}$ and $r_{6,14}$ are equivalent. For symmetry reduction from D_{6h} to C_s , the B_{2u} state is converted to an A" state. If the distances $r_{4,13}$ and $r_{6,14}$ are stepwise decreased under optimization of all

TABLE 2: Dihedral Angles (ϕ , deg) of Reactant,Intermediates, and Product of the Photocycloaddition ofEthene to Benzene

state	$R_0(D_{6h})$	$I_{0a}(C_s)$	I _{1b}	\mathbf{P}_0^a	\mathbf{P}_0^b
\$ 1234	0.0	13.1	-0.5	6.4	6.4
ϕ_{3216}	0.0	13.1	0.8	-54.5	-54.5°
ϕ_{3465}	180.0	-109.7	-118.4	-100.8	-100.8 ^d
ϕ_{34614}		116.9		101.4	101.4 ^e
\$65413		-45.4		-28.8	-28.8^{f}

^{*a*} Numbering as in figures. ^{*b*} Numbering as in figures. ^{*c*} ϕ_{2345} . ^{*d*} ϕ_{2356} . ^{*e*} ϕ_{21513} . ^{*f*} ϕ_{56114} .



Figure 5. Reaction scheme for the prefulvene mechanism.



Figure 6. Potential curves for the 1,3-photocycloaddition of ethene to benzene via prefulvene formation, optimized points of geometry in circles (\bigcirc) .

other coordinates, the intermediate $I_{0a}(A'')$ is reached. The large energy increase on the S_0 surface along this reaction pathway in the first step is due to the fact that all subsequent optimized points refer to the S_1 state. The excited state of benzene has a substantially different geometry from the ground state, and the energies of this state and all other states are vertical. Along this pathway to $I_{0a}(A'')$, a crossing to the S_0 state has taken place, whereby a reaction to P_0 can occur by closure of the $C^{(1)}-C^{(5)}$ bond. The barrier on the $S_1(A'')$ state surface is 1.22 eV with respect to the calculated vertical excitation energy so that a concerted 1,3-photocycloaddition of ethene to benzene via an exciplex mechanism can be excluded. It may, however, be possible that stepwise formation of I_{0a} would be easier than concerted.

3.2. Prefulvene Mechanism. After excitation to the $S_1(B_{2u})$ state, a prefulvene structure (I_{1b}) can be formed. Figure 5 shows a barrier of 0.26 eV in the S₁ state with respect to the calculated vertical excitation energy of benzene. In Figure 6, the corresponding potential curves are shown. Between $r_{46} = 1.8$ Å and $r_{46} = 1.7$ Å, an avoided crossing of HOMO and LUMO occurs. This leads to a discontinuity of the state energies at this point. This discrepancy is caused by the single determinant character of the SCF ground-state wave function. This leads to errors if topologically different orbitals are involved in the wave functions of the ground and excited states. To maintain continuity, a multiconfiguration self-consistent-field (MCSCF) procedure must be used.²⁰ An inconsistency of the CI due to HOMO-LUMO crossing leads to an increased barrier on the S₁ surface close to I_{1b} . We therefore estimate that I_{1b} can be formed from the $S_1(B_{2u})$ state of benzene. The main reaction coordinates in Figure 6 are the distances r_{46} until I_{1b} and the distances $r_{5,13}$

and $r_{1,14}$ from I_{1b} to P_0 . $r_{5,13}$ was optimized as all other coordinates from R_0 to $r_{5,13} = 2.5$ Å. At $r_{5,13} = 1.9$ Å, this bond also had to be kept fixed in the optimization, since the bond $C^{(1)}-C^{(14)}$ began to close.

If an ethene molecule is positioned above the intermediate I_{1b} at distances $r_{5,13} = 3.0$ Å and $r_{1,14} = 4.15$ Å (see Figure 5), IC to the ground state can take place. If $r_{5,13}$ is successively shortened under optimization of all other coordinates in the S₀ state, a $C^{(1)}-C^{(14)}$ bond is formed at a distance of 1.9 Å in the optimization process. The mechanism of the ethene addition to prefulvene intermediate I_{1b} occurs quasi-simultaneously. The steric information of substituents of ethene would therefore be conserved. This is in agreement with experiment. The barrier with respect to I_{1b} is only 0.2 eV. The total barrier from R_1 to TS is 0.46 eV, which is much smaller than the 1.22 eV in exciplex mechanism. However, if the reaction takes place in solution instead of the vapor phase considered here, collisional deactivation to the minimum on the S₁ surface would increase the barrier by another 0.73 eV. But this latter increase holds also for the exciplex mechanism.

4. Conclusion

In summary, we find that the concerted photocycloaddition via an exciplex is not possible due to the high barrier in the vapor phase. Here the 1,3-photocycloaddition of ethene to benzene should proceed via a prefulvene structure. The steric information of ethene is conserved. This is a consequence of the simultaneous or quasi-simultaneous addition of ethene to the intermediately formed prefulvene and is in agreement with experimental observations. In solution, both mechanisms involve deactivation. Both the concerted exciplex and the prefulvene mechanism are less likely. Therefore, we conclude that a nonconcerted exciplex mechanism must be involved to explain the experimental findings. Acknowledgment. The calculations were performed on the CYBER 180/995 and Siemens S400/40 at Universität Hannover. F. Neumann thanks Konrad-Adenauer-Stiftung for a predoctoral fellowship.

References and Notes

(1) Bryce-Smith, D.; Gilbert, A. Tetrahedron **1976**, *32*, 1309. Bryce-Smith, D.; Gilbert, A. Tetrahedron **1977**, *33*, 2459.

(2) Welzel, P. Nachr. Chem. Tech. Lab. 1983, 31, 262.

(3) Wilzbach, K. E.; Kaplan, L. J. Am. Chem. Soc. 1966, 88, 2066.
(4) Bryce-Smith, D.; Gilbert, A.; Orger, B. H. J. Chem. Soc., Chem. Commun. 1966, 512.

(5) Wender, P. A.; Howbert, J. J. J. Am. Chem. Soc. 1981, 103, 688.

(6) Wender, P. A.; Dreyer, G. B. Tetrahedron 1981, 31, 4445.

(7) Wender, P. A.; Dreyer, G. B. J. Am. Chem. Soc. 1982, 104, 5805.

(8) Wender, P. A.; Howbert, J. J. Tetrahedron Lett. 1982, 23, 3983.

(9) Dadson, M.; Gilbert, A.; Heath, P. J. Chem. Soc., Perkin Trans. 1 1980, 1314.

(10) Cornelisse, J. Chem. Rev. 1993, 93, 615.

(11) Nanda, D. N.; Jug, K. Theor. Chim. Acta 1980, 57, 95; Jug, K.; Iffert, R.; Schulz, J. Int. J. Quantum Chem. 1987, 32, 265; Li, J.; de Mello, P. C.; Jug, K. J. Comp. Chem. 1992, 13, 85.

(12) Buss, S.; Jug, K. J. Am. Chem. Soc. 1987, 109, 1044.

(13) Behrens, S.; Jug, K. J. Org. Chem. 1990, 55, 255.

(14) Jug, K.; Schluff, H.-P. J. Org. Chem. 1991, 56, 129.

(15) Müller-Remmers, P. L.; Mishra, P. C.; Jug, K. J. Am. Chem. Soc. 1984, 106, 2538.

(16) Jug, K.; Neumann, F. In *Theoretical Chemistry: Linking Theory* with Experiment; Montero, L., Smeyers, Y. G., Eds.; Kluwer: Dordrecht, 1992; S.92 f.

(17) Jug, K.; Neumann, F.; Schluff, H.-P. J. Org. Chem. 1993, 58, 6634.

(18) Gerwens, H.; Jug, K. J. Comput. Chem., in press.

(19) Neumann, F.; Jug, K. J. Org. Chem. 1994, 59, 6437. Neumann, F.; Jug, K. J. Org. Chem. 1994, 59, 6442.

(20) Werner, H. J.; Meyer, W. J. Chem. Phys. 1980, 73, 2342.

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