Mechanism of the Wolff Rearrangement

Minoru TSUDA* and Setsuko OIKAWA

Laboratory of Bio-physical Chemistry, Faculty of Pharmaceutical Sciences, Chiba University, Chiba 260, Japan. *Received September 12, 1988*

The direct formation of ketene occurs in a concerted fashion with the nitrogen loss reaction in the Wolff rearrangement of both cyclic and open-chain 2-diazoketones. The mechanism proposed the previous paper generalized to cover a wider range of experiments. No ketocarbene intermediate is produced in any case.

Keywords Wolff rearrangement; reaction mechanism; oxirene; ketene; triplet state ketocarbene; 2-diazoethan-1-one; molecular orbital method; potential energy hypersurface

Introduction

In the previous paper,[1] we proposed a new mechanism of the Wolff rearrangement on the basis of the potential energy hypersurfaces of cyclic and open-chain 2-diazoketones (Fig. 1). In the case of 2-diazobenzen-1-one, its nitrogen loss reaction takes place simultaneously with the Wolff rearrangement in a concerted fashion and neither ketocarbene nor oxirene is produced (route (a) in Fig. 1). In contrast to the cyclic 2-diazoketone, 2-diazoethan-1-one, an open-chain 2-diazoketone, produces oxirene through its nitrogen loss reaction in a concerted fashion and the oxirene isomerizes to ketene *via* the Wolff rearrangement (route (b) in Fig. 1). Recently, we have found that route (a) in Fig. 1 is also effective for an open-chain 2-diazoketone. Thus, an open-chain 2-diazoketone has two routes of the Wolff rearrangement, *i.e.*, the direct formation of a ketene in one step and the indirect formation *via* an oxirene intermediate.

The mechanism of the Wolff rearrangement proposed in the previous paper[1] is generalized by this finding to cover a wider range of experiments. Various ^{13}C labeling studies have been carried out with symmetrically substituted open-chain 2-diazoketones. Strausz *et al.* reported that 1,2-dimethyl-2-diazoethan-1-one produced equal amounts of ketenes with and without migrated oxygen in gas phase photolysis.[2] This result implies 100% participation of the oxirene intermediate in the Wolff rearrangement. However, photolyses of 1,2-diphenyl-2-diazoethan-1-one in cyclopentane and in dioxane–water (2 : 1) led to values of 54% and 46% for oxirene participation, respectively.[3] Moreover, Franzen found no oxirene participation in photolysis or thermolysis of the same compound by ^{14}C-labeling studies.[4] Provided that the mechanism in Fig. 1 is valid, these conflicting experiments can be explained in trivial terms of solvent effects, experimental conditions, *etc.*, because the activation energy of the nitrogen elimination of an open-chain 2-diazoketone has an approximately equal value in both routes (a) and (b), as shown later.

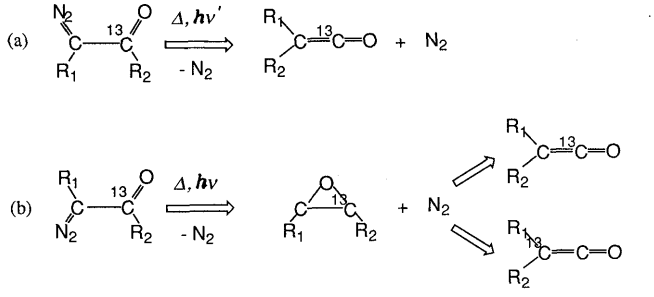

Fig. 1. Mechanism of the Wolff Rearrangement: No Ketocarbene Intermediate is Produced in Any Case

(a) The direct formation of ketene, the *cis*-conformation refers to both cyclic and open-chain 2-diazoketones. Ketene is the one-step reaction product in this route, where no scrambling of ^{13}C takes place. (b) The route *via* oxirene intermediate. An oxirene intermediate is produced only in the case of open-chain 2-diazoketones (from that of *trans*-conformation), where scrambling or oxygen atom migration is observed.

Method

Details of the method of calculation were presented in the previous paper.[1] The determination of the lowest energy path was carried out by the calculation of the intrinsic reaction coordinate (IRC) on the 3N-6 dimensional hypersurface.[5] The geometries at the minima (the stable structure) as well as at the saddle point (the transition state structure) of the reaction system were fully optimized,[6] and confirmed by vibrational analysis.[7] For the potential energy evaluation in the geometry optimization and IRC calculations, the spin-restricted Hartree Fock (RHF) molecular orbital method was adapted with the semi-empirical MINDO/3[8] parametrization. The potential energy surfaces were elaborated with configuration interaction (CI) calculations,[9] which consider the singly and doubly excited electronic configurations less than 14 eV from the ground state (SD-CI). The potential energy change obtained in the previous paper[1] by the same method of calculation on the reaction path from oxirene to ketene in the case of 2-diazoethan-1-one is very similar to the results obtaine by an *ab initio* method with configuration interaction.[10] Thus, the results obtained in the present calculations should be reliable, at least qualitatively.

Results and Discussions

Potential Energy Change Following the Lowest Energy Path of the Direct Formation of Ketene from 2-Diazoethan-1-one The potential energy change following the lowest energy path of the nitrogen loss reaction of 2-diazoethan-1-one is shown in Fig. 2 in the case of direct formation of ketene (route (a) in Fig. 1). The Wolff rearrangement to

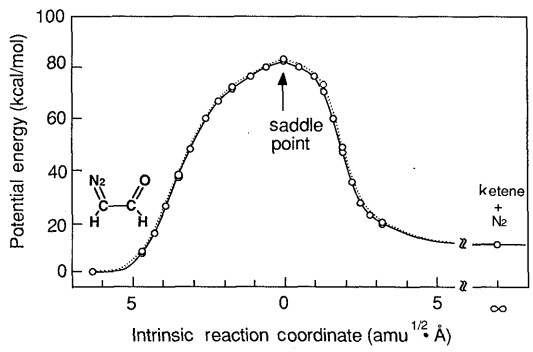

Fig. 2. Potential Energy Change Following the Lowest Energy Path of the Nitrogen Loss Reaction of 2-Diazoethan-1-one in the Direct Formation of Ketene

——, by MINDO/3; – – – –, by SD-CI.

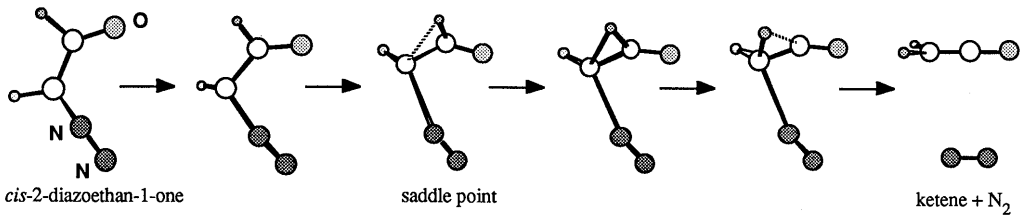

Fig. 3. The Molecular Structure Change of 2-Diazoethan-1-one along the Lowest Energy Path of Direct Ketene Formation

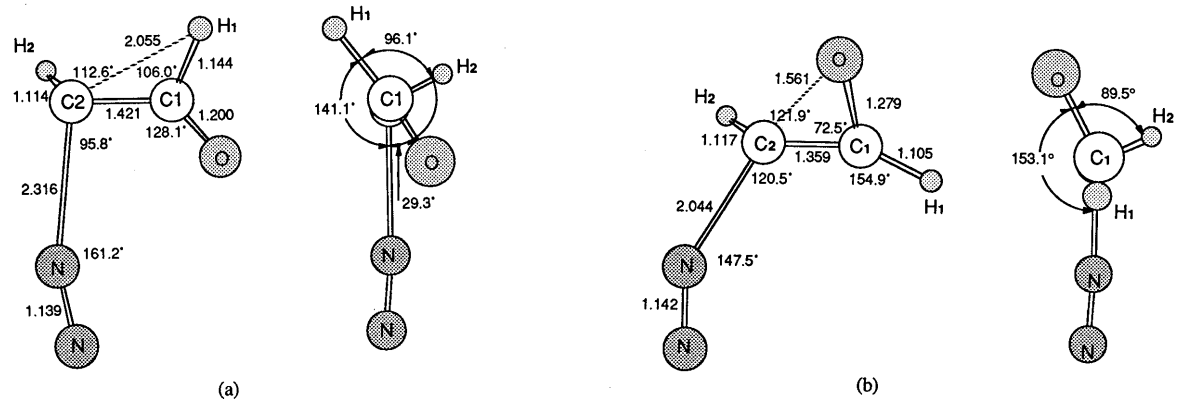

Fig. 4. The Saddle Point Structures in (a) the Direct Formation of Ketene (the Route of Fig. 1(a)) and (b) the Formation of Oxirene Intermediate (the Route of Fig. 1(b))

ketene occurs simultaneously with the nitrogen molecule liberation in a concerted fashion. The reaction takes place in one step and neither ketocarbene nor oxirene is produced.

Molecular Structure Change of 2-Diazoethan-1-one along the Lowest Energy Path of the Direct Formation of Ketene The molecular structure change of 2-diazoethan-1-one along the lowest energy path of the direct formation of ketene is shown in Fig. 3. The structure at the saddle point is non-planar as indicated in Fig. 4(a), which is different from the saddle point structure leading to oxirene (Fig. 4(b))[1]; *i.e.*, the oxygen atom forming a three-membered ring of Fig. 4(b) is replaced by the hydrogen atom H_1 in Fig. 4(a) and the ring becomes loose. It seems likely that the oxygen produces a stable three-membered ring, oxirene, because of the bivalency of oxygen in the route of the Wolff rearrangement leading to the oxygen migration, but the hydrogen H_1 is transferred from the carbon C_1 to the carbon C_2, because of the monovalency of hydrogen in the route of direct formation of the ketene.

In contrast to the *trans*-conformation in the route with the oxirene intermediate participation, the IRC calculation from the saddle point structure of Fig. 4(a) leads to the *cis*-conformation of 2-diazoethan-1-one as the starting compound in the route of direct formation of the ketene (Fig. 3). *cis*-2-Diazoethan-1-one is more stable than its *trans*-conformational isomer and the activation energy for the *cis–trans* isomerization is about 0.5 kcal/mol.[1] Moreover, the activation energies are 80 kcal/mol for oxirene formation[1] and 83 kcal/mol for the direct formation of ketene. These results suggest that an open-chain 2-diazoketone is not always planar in ordinary experiments, and a slight change of reaction temperature or the solvent effect, *etc.* gives a different value of oxirene participation. Since cyclic 2-diazoketone always has *cis*-conformation. we can conclude that route (a), direct formation of ketene, originates from the *cis*-conformation and route (b), with oxirene participation, from the *trans*-conformation.

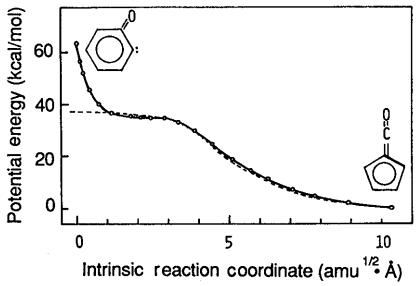

Fig. 5. The Lowest Energy Path Starting from a Postulated Singlet Ketocarbene Structure Formed from 2-Diazobenzen-1-one

No ketocarbene structure has a minimum on its potential energy hypersurface. At the potential energy minimum, the ketocarbene structure vanishes and a ketene structure is generated. The dotted line is the IRC for the nitrogen loss reaction of 2-diazobenzen-1-one in the previous paper.[1]

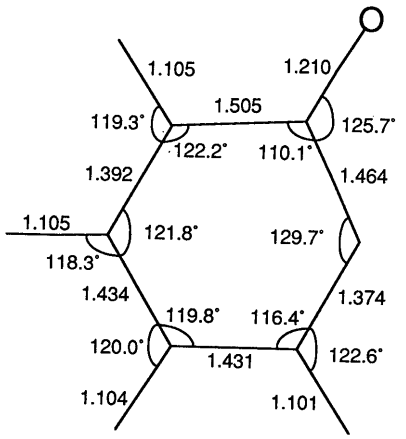

Fig. 6. The Stable Structure of Ketocarbene in the Triplet State Generated from 2-Diazobenzen-1-one

Ketocarbene Formation in the Lowest Triplet State No ketocarbene is formed on the potential energy hypersurface in the lowest singlet state as indicated above. When an IRC calculation was started from a postulated ketocarbene structure in the lowest singlet state, obtained from 2-diazobenzen-1-one by removing the N=N group, the lowest potential energy path led to the structure of ketene spontaneously, as shown in Fig. 5. However, the same calculation on the lowest triplet state potential energy hypersurface reached a minimum point corresponding to a ketocarbene structure. Its optimized structure is shown in Fig. 6. Chapman *et al.* identified the triplet state aromatic ketocarbene in 10—15 K argon matrix.[11] The structure of the keto-carbene in the triplet state that originated from 2-diazoethan-1-one was reported by Tanaka *et al.*[12]

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