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Reaction Pathways for Various Ketene Dimers*

Karl Jug and C. P. D. Dwivedi**

Theoretische Chemie, Technische Universität Hannover, Callinstr. 3A, D-3000 Hannover,
Federal Republic of Germany

James S. Chickos

Department of Chemistry, University of Missouri, St. Louis, USA

Alternative pathways for the thermolysis of diketene were investigated with a semiempirical SINDO method [1]. Transition states and activation energies for isomerization to cyclobutane-1,3-dione and 2,4-dimethylene-1,3-dioxetane were determined. The dissociation and formation of these three dimers into and from two ketenes was also calculated. The results disclose the possibility of existence of intermediates as well as the fragmentation into further products. Entropy appears as a major factor in this reaction at higher temperature.

Key words: Ketene dimers, thermolysis of ~

1. Introduction

The understanding of chemical reactions on the basis of quantum chemistry has greatly advanced in the last decade. In particular, it is now possible to determine transition state geometries and activation energies for sufficiently simple systems. One problem, however, still remains to be solved: how to predict the products of reactants if various possibilities for product formation from a given set of reactants exist. This situation is entirely different from that of an experimentalist who lets the reaction occur and then by analysis determines the nature of the products. Even in the gas phase the possibilities for product formation can be quite complicated. We want to demonstrate this in the case of diketene. It is well known that the dimerization of two ketenes yields diketene [2] whereas di-substituted ketenes combine to form cyclobutane-1,3-diones [3]. These investigations were mainly in solution. We have previously dealt with the theoretical treatment of mechanistic pathways of ketene dimerization [4] and with the experimental investigation of the

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** Permanent address: Department of Physics, Gorakhpur University, India.

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thermolysis of diketene in the gas phase [5]. In this contribution we wish to raise the question of alternative pathways. In the following sections both isomerization and dissociation of diketene are considered. Transition state geometries and activation energies are determined with semiempirical SCF CI calculations [1]. Possibilities for conversion and fragmentation are discussed.

2. Structure of Ketene and Its Dimers

The geometry of ketene, diketene, cyclobutane-1,3-dione and 2,4-dimethylene-1,3-dioxetane was optimized with respect to all internal coordinates with SINDO closed-shell SCF calculations. We then included a limited CI with 13 configurations including those single and double excitations from the four highest occupied to the four lowest unoccupied MO's which gave significant contributions to the correlation energy of the above compounds in their equilibrium and transition states and allow to check for degeneracies. Two ketenes were calculated to be 38 kcal/mole higher in energy, cyclobutane-1,3-dione 6 kcal/mole higher and 2,4-dimethylene-1,3-dioxetane 12 kcal/mole lower than diketene. From heats of formation for ketene and diketene [6, 7] two ketenes are found to be 23 kcal/mole [6] higher in energy than diketene. Cyclobutane-1,3-dione and diketene appear to have comparable stabilities [5]. The calculations appear to overestimate the stability of the lactone dimer and underestimate the stability of cyclobutane-1,3-dione. No experimental data are available for 2,4-dimethylene-1,3-dioxetane. Since our calculations appear to underestimate the CO double bond strength by about 10 kcal/mole all three isomers should have comparable ground state energies. The following discussion refers to reactions presented in Fig. 1. It is apparent that the isomerization of diketene to the 1,3-dione and the 1,3-dioxetane involves the breaking and formation of one bond only. We have not considered the conversion of three other isomers of diketene, namely cyclobutane-1,2-dione, 3,4-dimethylene-1,2-dioxetane and 2-methyleneoxetan-3-one since they are not directly accessible by isomerization of diketene. Diketene, cyclobutane-1,3-dione

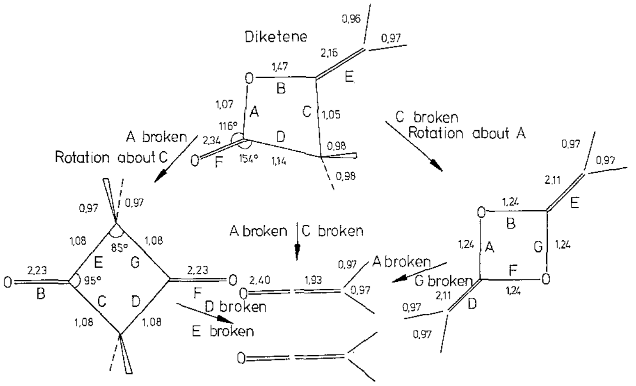


Fig. 1. Molecular shape and bond orders of ketene, diketene, cyclobutane-1,3-dione, 2,4-dimethylene-1,3-dioxetane

and 2,4-dimethylene-1,3-dioxetane can dissociate into two ketenes by breaking two bonds. We have not included other possible isomers which cannot dissociate into two ketenes.

In this figure we do not list bond lengths and bond angles which have the usual errors of SINDO calculations tested [1], i.e. the bond lengths are 9% too long and the bond angles incorrect by a few degrees. Instead we emphasize the importance of bond orders for reactions. The bond orders are calculated by a maximum bond order principle [8] which was successfully applied previously for reactions [9]. It was also shown that bond orders do not change significantly when comparable *ab initio* calculations are performed instead of SINDO calculations or if experimental geometries are used [10]. We therefore can rely on bond orders as one means of understanding reactions. From Fig. 1 it is apparent that the weakest ring bonds in diketene are *A* with 1.07 and *C* with 1.05. Breaking of bonds *B* and *D* with bond orders of 1.47 and 1.14 respectively, which would lead to CO_2 and allene, should involve a higher activation energy. In cyclobutane-1,3-dione all four ring bonds have bond order 1.08 similar to cyclobutane. However, the ring has a rhombus form. 2,4-dimethylene-1,3-dioxetane has four equal ring bonds and the ring forms a square. Consequentially *A* and *G* or *B* and *F* could be broken to yield two ketenes.

3. Isomerization of Diketene

The dihedral angle of bonds *B*, *C*, *D* has been used as an angle of the rotation about bond *B*. This angle is 0° for diketene and 180° for cyclobutane-1,3-dione. Figure 2 shows the energy profile for a reaction along this coordinate with the energy

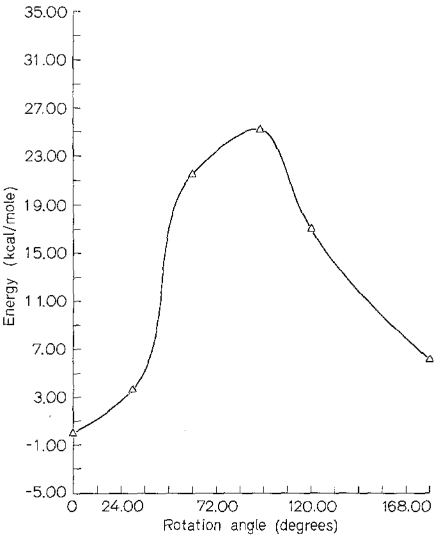


Fig. 2. Energy profile in dependence of dihedral angle of rotation for diketene cyclobutane-1,3-dione isomerization with all other coordinates optimized. △ – Energy (kcal/mole)

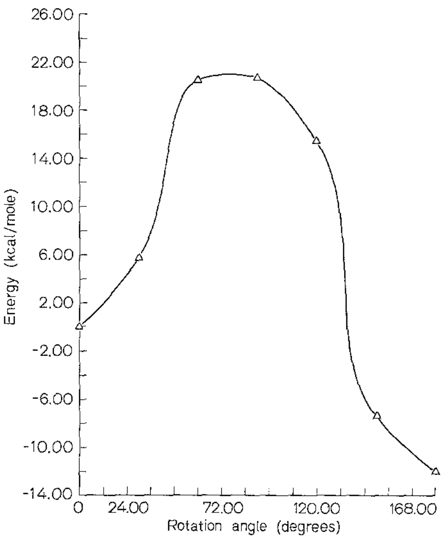
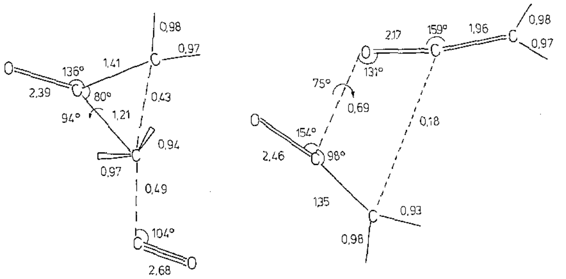


Fig. 3. Same as Fig. 2 for diketene 2,4-dimethylene-1,3-dioxetane isomerization. △ – Energy (kcal/mole)

minimized for each point with respect to all other internal coordinates. The transition state is reached at a dihedral angle of 94° and lies approximately 26 kcal/mole above diketene. The transition state is a saddle point on the hypersurface without diradical character. The direction of vector belonging to the only negative root of the force constant matrix at the transition state involves the dihedral angle of *B*, *C* and *D* and the bond angle of *B* and *C*. For conversion of diketene to 1,3-dioxetane the energy plot is presented in Fig. 3. The rotation angle is defined as the dihedral angle of bonds *B*, *A*, *D* of Fig. 1. It is 0° for diketene and 180° for 1,3-dioxetane. The transition state occurs at 75° and the barrier is 22 kcal/mole. Since CI significantly changed the location of the transition state, we could not determine its geometry with the same accuracy as in the diketene → cyclobutane-1,3-dione case. In particular no information about the direction of ascent to the transition could be easily obtained. Furthermore the exact magnitude of the barrier could be substantially higher. The geometries of the transition states are depicted in Fig. 4 with



Diketene → Cyclobutane-1,3-dione   Diketene → 2,4-Dimethylene-1,3-dioxetane

Transition States

Fig. 4. Molecular shapes and bond orders of transition states for diketene dione and diketene dioxetane isomerization

bond orders characterizing the bonds. The following conclusions seem possible. The conversion of diketene to 1,3-dione passes by a region on the hypersurface in which dissociation to CO and cyclopropanone might occur. Conversion of diketene to 2,4-dimethylene-1,3-dioxetane seems to loosen bond *A* and this may lead to dissociation to two ketenes. Figures 5 and 6 show the variation of the bond orders along these pathways. In Fig. 5 the OC double bond *B* of the dione is formed early, whereas the CC double bond *E* of diketene is stepwise loosened and then broken. Intermediately a sizeable CC cross bond is formed towards cyclopropanone. In Fig. 6 on the way from diketene to 2,4-dimethylene-1,3-dioxetane an OC double bond *B* is formed intermediately which has to be converted finally into a single bond again. The CC single bond *D* is converted stepwise into a double bond. Most remarkable is the intermediate weakening of the CC bond *A* about which rotation occurs. The conclusion of this investigation is that isomerizations are energetically forbidden and even if the barriers are surpassed dissociation into fragments might occur.

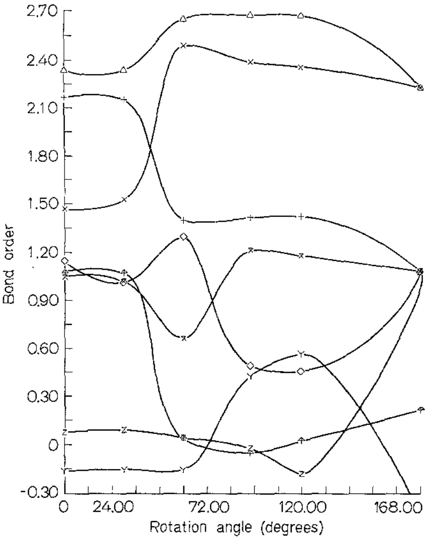


Fig. 5. Bond orders accompanying energy profile of Fig. 2. Δ – O=C; + – C=C; X – O–C; ◇ – C–C; ↟ – O–C; X̄ – C–C; Z – C·C; Y – C·C

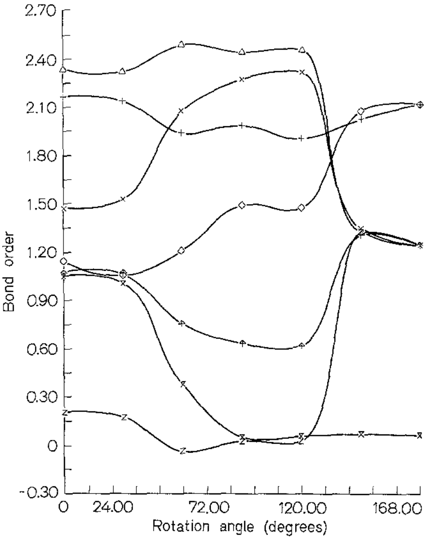


Fig. 6. Bond orders accompanying energy profile of Fig. 3. Δ – O=C; + – C=C; X – O–C; ◇ – C–C; ↟ – O–C; X̄ – C–C; Z – O·C

4. Dissociation of Isomers

The rate-determining step in the dissociation of diketene into two ketenes should be the breaking of the stronger one of the two bonds *A* and *C*, namely *A*. From experimental data we could not give preference to *A* or *C* with regard to the rate-determining step [5]. We therefore chose the bond length *A* as a guiding coordinate along which the energy was minimized with respect to the rest of the

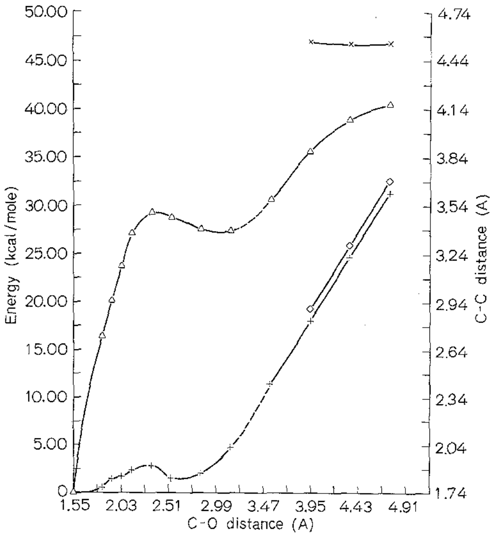


Fig. 7. Energy profile for diketene ↔ 2 ketene reaction. Δ – energy (kcal/mole) dissociative; + – C–O distance (*A*) dissociative; X – energy (kcal/mole) formative; ◇ – C–O distance (*A*) formative

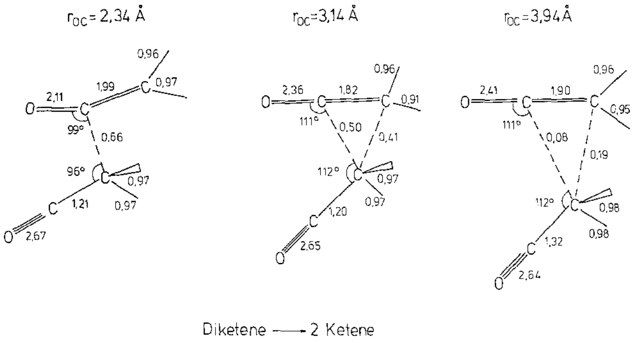


Fig. 8. Molecular shapes and bond orders for three representative stages during diketene ↔ 2 ketene reaction

internal coordinates. This energy plot is presented in Fig. 7. Three steps can be distinguished. The breaking of CO bond *A*, the subsequent breaking of bond *C* without internal rearrangement of the two ketenes and the internal rearrangement of the two ketenes to their equilibrium geometry. Behaviour of bond length *C* is presented in the lower portion of the graph. Steps 1 and 2 are separated by a dashed line. Steps 2 and 3 are described by curves on top of each other. We call step 2 dissociative and step 3 formative, because the latter looks alike to the approach of two non-vibrating but energetically interacting ketenes. Most remarkable is the formation of an intermediate at $r_{CO} = 3.14$ Å after bond *A* is broken. Also the formative approach of two ketenes is at higher energies than the dissociation without rearrangement. The slope of the upper curve is small. Figure 8 characterizes three stages along this path. The intermediate is characterized by a cyclopropenyl formation. The estimated barrier can be between 44 and 47 kcal/mole.

The energy plot for dissociation of 1,3-dione in Fig. 9 looks quite different. No

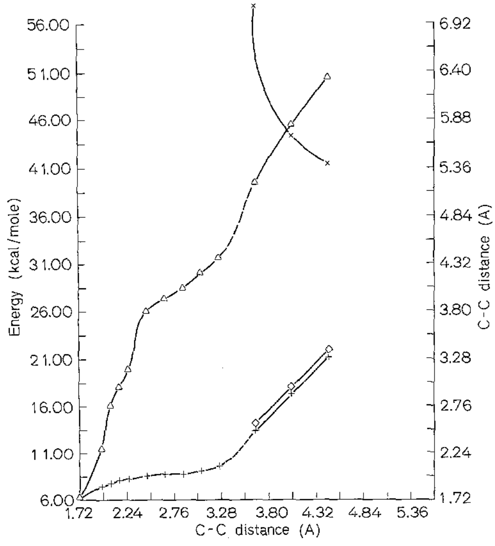


Fig. 9. Same as Fig. 7 for cyclobutane-1,3-dione ↔ 2 ketene reaction △ – energy (kcal/mole) dissociative; + – C–C distance (*A*) dissociative; × – energy (kcal/mole) formative; ◇ – C–C distance (*A*) formative

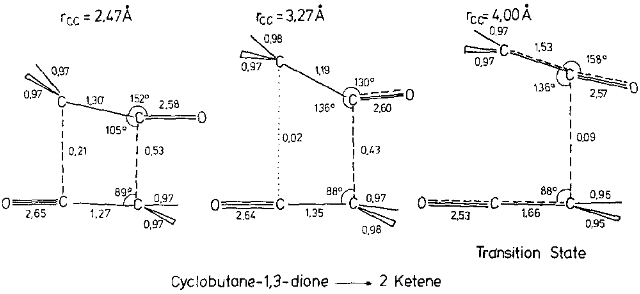


Fig. 10. Same as Fig. 8 for cyclobutane-1,3-dione ↔ 2 ketene reaction

formation of an intermediate occurs. The dissociative and formative curves intersect, so that a transition can clearly be located at a CC distance E of 4.00 Å. The activation energy is about 39 kcal/mole, i.e. 45 kcal/mole above diketene. The slope of the formative curve is much higher than in diketene. Three representative stages along this reaction pathway are in Fig. 10. One bond is broken whereas the second one is loosened before breaking.

The energy plot for dioxetane in Fig. 11 shows again an intermediate but also two barriers at 54 kcal/mole, i.e. 42 kcal/mole above diketene. The approach of two non-vibrating ketenes from this direction would yield an intermediate attractive region before strong repulsion sets in. The three characteristic stages are in Fig. 12. The first barrier shows when two OC single bonds are loosened and partial π-bonds are formed in the remaining two OC bonds. The energy is lowered again by breaking one single OC bond and so letting the π-bonds form more freely. Most remarkable is the energy lowering at $r_{CO} = 3.11$ Å with a head-on approach of the negative O atom toward the positive C atom of the other ketene.

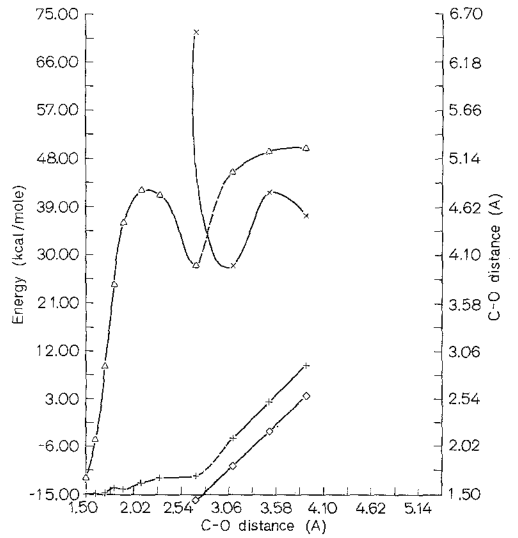
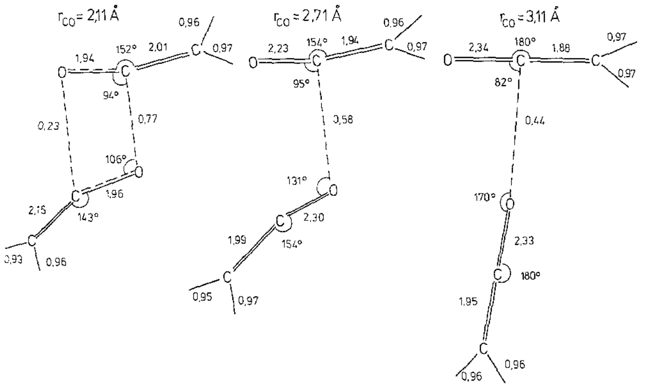


Fig. 11. Same as Fig. 7 for 2,4-dimethylene-1,3-dioxetane ↔ 2 ketene reaction △ – energy (kcal/mole) dissociative; + – C–C distance (A) dissociative; × – energy (kcal/mole) formative; ◇ – C–C distance (A) formative



2,4-Dimethylene-1,3-dioxetane → 2 Ketene

Fig. 12. Same as Fig. 8 for 2,4-dimethylene-1,3-dioxetane ↔ 2 ketene reaction

If we compare the structural isomerization of the dimers with their dissociation, activation energies for the former reactions are lower by almost 20 kcal/mole in the present calculation. These values seem to be too low. Yet the rate is determined by the free energy [11]. It is well known that the entropy of two fragments is higher than that of the united compound thus reducing the free energy of the compound and shifting the rate favourably toward the fragments. In cyclobutane dissociation at 800° K this shift of the free energy due to entropy is 32 kcal/mole [12] favouring formation of two ethylenes in an otherwise endothermic reaction. In this work the situation is very similar and we expect the free energy of two ketenes to be lower than any of the dimers. This would also explain why thermolysis of diketene into two ketenes was more easily achieved than dimerization of ketene [5] at high temperature. Furthermore the barrier for dissociation as compared to structural isomerization should be more reduced by entropy, because the former transition states have a higher degree of random structure and consequently higher entropy. The potential surface for 2 ketene → diketene formation is quite flat compared to the two other possibilities of dimerization which were considered. This comparatively higher randomization, hence higher entropy would reduce the barrier of this process more than in the other cases. This would explain why diketene is primarily formed from two ketenes. Just recently it has been found that besides diketene cyclobutane-1,3-dione has been formed in about 4% [13]. The latter compound may isomerize to its enol form.

5. Conclusion

An investigation of the possibilities of isomerization and dissociation of various ketene dimers yielded new insight into the problems of alternative pathways on a hypersurface. Isomerization is forbidden not only by energy barrier considerations but also by the possibility of fragmentation. Transition states were saddle points on the hypersurface. Dissociation of diketene and its isomers may lead through pathways with bond-breaking of one bond and bond-loosening of the other. So the bond-breaking of the two bonds involved is not synchronous, but still concerted. Furthermore, in the case of diketene and dioxetane intermediates might be formed. Diradicals were not found important in the mechanism of these reactions. Activation energies for dimerization to the three dimers are estimated to be of the same magnitude. A preference for diketene formation from two ketenes might be possible due to the smaller increase in slope of the potential curve upon approach of the two ketenes compared with the two other cases. This means that the entropy is comparatively higher thus reducing the free energy and enhancing the rate more.

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