METHYLENE PRODUCED BY VACUUM ULTRAVIOLET PHOTOLYSIS. ENERGY OF THE METHYLENE

A. K. DHINGRA, J. H. VORACHEK and R. D. KOOB Department of Chemistry, North Dakola Slate University, Fargo, North Dakota 58102, USA

Received 12 February 1971

Unimolecular rate constants have been determined for the decomposition of n- and *iso*-butane produced by the insertion of methylene into propane. Methylene was produced by the photolysis of propane at 123.6 nm and cyclopropane at 165 nm. From these rate constants estimates have been made of the energy carried to the insertion reaction by the respective methylenes. These estimates provide the first indication of how energy is partitioned in the photolysis of small hydrocarbon molecules.

.

The energy associated with methylene produced by the vacuum ultraviolet (VUV) photolysis of small hydrocarbon molecules is of interest for several reasons. The fate of the rather large amounts of excess energy deposited in the photolyzed molecule has not been elucidated. Little is known about partitioning of this energy among the fragments produced in the photolysis, or in what degrees of freedom the partitioned energy is likely to be deposited.

Methylene generated by the photolysis of ketene or diazomethane at several wavelengths has been used as a reactant to produce chemically activated species [1,3]. Small hydrocarbons, especially cyclopropane, may be useful in extending this technique to higher energy ranges. Perhaps more important is the observation that certain of the reactions of methylene, notably the insertion of methylene into C-H bonds, have been found to be energy independent [2,3]. The range of energies over which such reactions show no dependence has not been determined at this time. Since the methylenes produced by VUV photolysis of propane and cyclopropane fall into the energy independent category for this reaction, it is important to determine the energy carried by these methylenes.

We have determined unimolecular rate constants for the dissociation of butanes formed by the insertion of singlet methylene into propane. The singlet methylene was generated by the photolysis of propane at 123.6 nm and the photolysis of cyclopropane at approximately 165 nm.

The first photolytic reaction is 98 kcal endothermic, leaving 133 kcal to be distributed between the fragments, ethane and methylene. The second photolytic reaction is 93 kcal endothermic, leaving 80 kcal to be distributed among the products, ethylene and methylene. Thus, significant amounts of energy may be carried by methylene whether generated from propane or cyclopropane.

The methylene insertion reaction into propane is 100 kcal exothermic (forming isobutane). The butane formed will carry this energy plus whatever energy is brought to the reaction complex by the reactants. Only thermal energy will be contributed by the propane and significant energy in excess of the exothermicity of the reaction must be ascribed to the methylene. Both kinetic energy and internal energies of the methylene will contribute to this excess. The rate of unimolecular dissociation of the butane will presumably reflect the total energy of the butane.

Johnson et al. (JHS) have measured unimolecular rate constants for the dissociation of isobutane formed by the insertion of methylene into propane [3]. They generated methylene by the photolysis of diazomethane at 435.8 nm and 366.0 nm respectively. For the isobutanes resulting from the methylene insertion at each wavelength, they measure dissociation rate constants of 1.9×10^7 sec⁻¹ and 3.6×10^7 sec⁻¹, respectively. JHS then calculate the dissociation rate constant as a function of energy of isobutane.

17



 $\omega^{-1} \times 10^{9}$

Fig. 1. $\bullet - [C_2H_4]/[i-C_4H_{10}]$. cyclopropane photolysis. $\Box - [C_2H_6]/[i-C_4H_{10}]$, propane photolysis. Collision frequency used to calculate ω was 10⁷ torr-1 sec⁻¹. Rate constants quoted in the text are slope/intercept of these plots.

In the photolysis of propane and cyclopropanepropane mixtures, rate constants for the dissociation of methylene produced isobutane are calculated from the data of fig. 1 to be 8.2×10^7 sec⁻¹ and 7×10^7 sec⁻¹, respectively. When these points are placed on the calculated curve of JHS, they correspond to total isobutane energies of 132 kcal and 131 kcal. Assuming the correctness of the energy axis of the calculation of JHS, this corresponds to energies carried by the methylene produced in the VUV of 32 kcal for propane and 31 kcal for cyclopropane.

Even if one is not willing to grant that the absolute values of the energies of VUV produced methylenes are correct. it is probably quite safe to conclude that the VUV produced methylenes carry approximately 1.5 times as much energy as those methylenes produced in the diazomethane photolysis. This, in turn, implies that a considerable fraction of the excess energy remaining after the primary photodecomposition of propane and cyclopropane goes to the methylene. More, in fact, than might have been predicted on the basis of statistical energy partiticning. This last aspect is presently under study and will be the subject of future reports.

The authors would like to thank the National Science Foundation for partial support of this work.

REFERENCES

J.D. Rynbrandt and B.S. Rabinovitch. J. Phys. Chem. 74 (1970) 1679 and references therein: W.G. Clark, D.W. Setser and E.E. Siefert, J. Phys. Chem. 74 (1970) 1670 and references therein; J.W. Simons and G.W. Taylor, J. Phys. Chem. 73

J.W. Simons and G.W. Taylor, J. Phys. Chem. 73 (1969) 1274 and references therein.

- [2] A.K.Dhingra and R.D.Koob, J. Phys. Chem. 74 (1970) 4490.
- [3] R.L.Johnson, W.L.Hase and J.W.Simons, J. Chem. Phys. 52 (1970) 3511.