CROATICA CHEMICA ACTA CCACAA **56** (2) 185—190 (1983)

YU ISSN 0011-1643
CCA-1367 UDC 541.124:547
Original Scientific Paper

SCF-Calculations as Tool to Interprete Reaction Pathes — The Cases of CO_2 Loss from Ionized $ClCH_2—COOCH_3$ and C_2H_4 Loss from Ionized $(CH_3)_2N—COCH_2X$*

Gernot Frenking and Helmut Schwarz*

Institut für Organische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, D-1000 Berlin 12, W.-Germany

Received August 30, 1982

The localization of transition states as saddle points having one negative eigenvalue of the force-constant matrix provides important informations on the energy hyperface of chemical reactions. It can be used for determining the reaction path of unusual experimental results and is demonstrated for the title reactions.

DETAILS OF CALCULATIONS

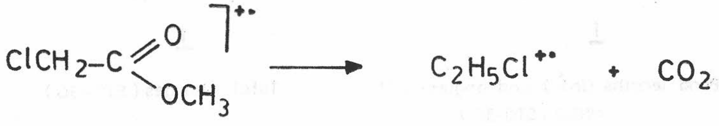
All semi empirical calculations have been performed by the MNDO[1] method with complete optimization of all geometrical parameters. Transition states have been located by minimization of the gradient norm.[2] Ab initio calculations were done with Gaussian 76.[3]

EXPERIMENTAL DETAILS

All experiments were conducted in a mass spectrometer. By using techniques like collision-activation (CA) mass spectrometry, isotope labeling and analysis of metastable peaks the energetic course and identity of the products of the unimolecular reactions is known to some degree. For more details, see refs. 4 and 5.

CO_2 LOSS FROM IONIZED $ClCH_2—COOCH_3$[4]

The following reaction has been investigated:



(1)

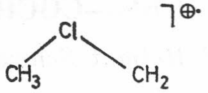
A comparison of the CA-spectrum of $C_2H_5Cl^{+\cdot}$ from reaction (1) with that from ethylchlorid$^{+\cdot}$ revealed that the structures must be different. SCF calculations on possible alternatives yielded a surprisingly stable, bridged structure

---

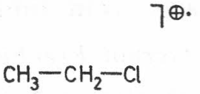
* Presented at *The IUPAC International Symposium on Theoretical Organic Chemistry,* held in Dubrovnik, Croatia, August 30 — September 3, 1982.

TABLE I

Structure and Energies of $C_2H_5Cl]^{\oplus\cdot}$

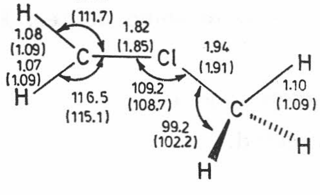


1



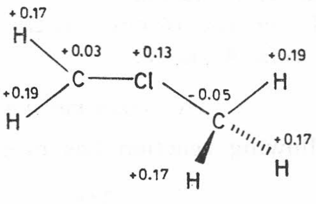
2

	1	2	ΔE(kcalmol^{-1})
ΔH$_f$ (MNDO) [kcalmol^{-1}]	235.1	245.2	10.1
E(STO-3G/STO-3G) [a.u.]	-531.9532	-531.9732	-12.5
E (4-31G/STO-3G) [a.u.]	-537.1310	-537.1455	-9.0
E (UMP2/6-31G*//STO-3G) [a.u.]	-538.131	-538.142	-6.4



1

Bond lengths (in Å) and angles (in°)
MNDO (STO-3G)

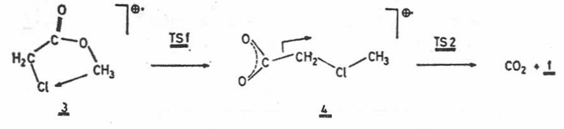


1

Total charges (STO-3G)

as shown in Table I. MNDO predicts the bridged structure to be even more stable by 10 kcal/mol, whereas the best ab initio data show a reverse stability but the difference is merely 6.4 kcal/mol. There is no doubt that structure **2** is produced in reaction (1).

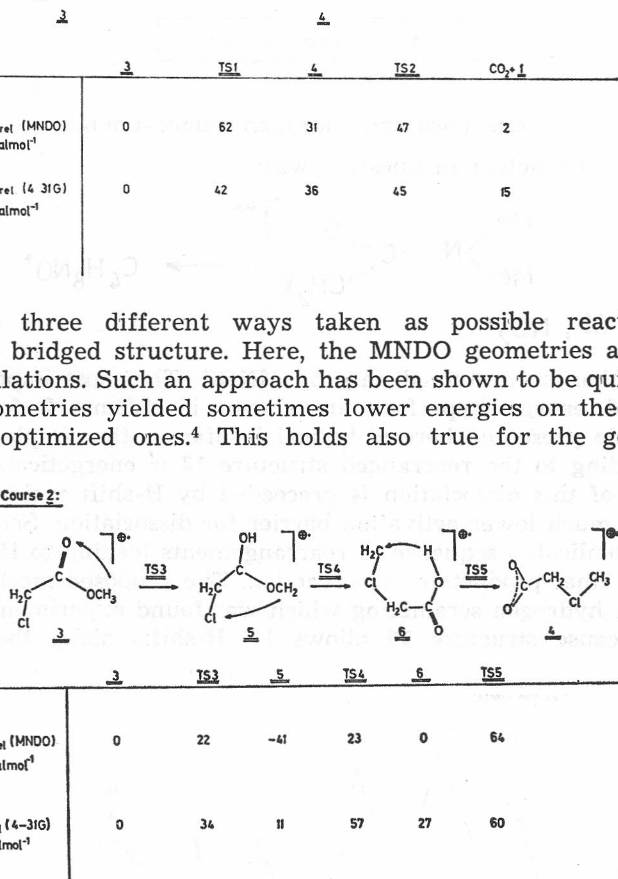
Course 1:



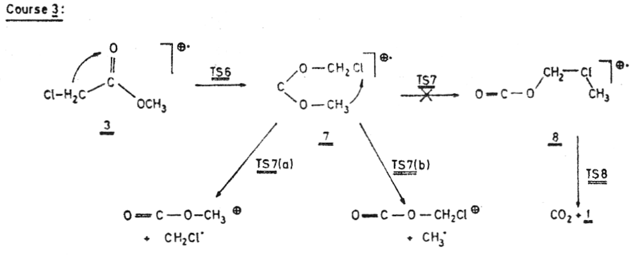
	3	TS1	4	TS2	CO_2+ 1
ΔE_{rel} (MNDO) kcalmol^{-1}	0	62	31	47	2
ΔE_{rel} (4 31G) kcalmol^{-1}	0	42	36	45	15

There are three different ways taken as possible reaction courses to produce the bridged structure. Here, the MNDO geometries are taken for the 4-31G calculations. Such an approach has been shown to be quite reliable,[5b] the MNDO geometries yielded sometimes lower energies on the 4-31G level than STO-3G optimized ones.[4] This holds also true for the geometries of transition states as shown for the keto-enol tautomerism of radical cations.[6] The data in course 1 indicate that structure **4** is the imidiate precursor for the bridged structure and that **4** is most probably produced via reaction course 1. In reaction course 3, the activation barriers **7**(a) and **7**(b) are calculated to be less than 5 kcal/mol by both methods due to the weak O—CH_3 and O—CH_2Cl bonds. This inhibits building of **8** and discriminates thereby course 3 as reaction path towards structure **1**.

Course 2:



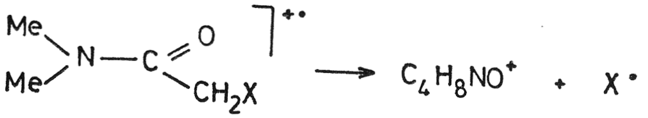
	3	TS3	5	TS4	6	TS5
ΔE_{rel} (MNDO) kcalmol^{-1}	0	22	-41	23	0	64
ΔE_{rel} (4–31G) kcalmol^{-1}	0	34	11	57	27	60



TS 7(a), TS 7(b) « TS 7

C_2H_4 LOSS FROM IONIZED $(CH_3)_2N—COCH_2X$[5]

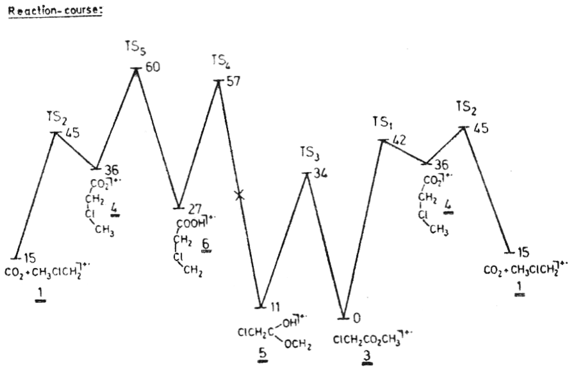
The second reaction in question was:

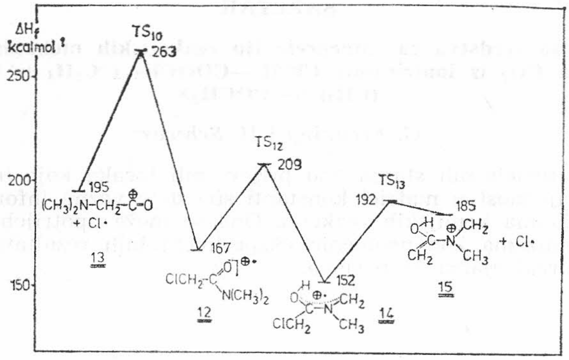


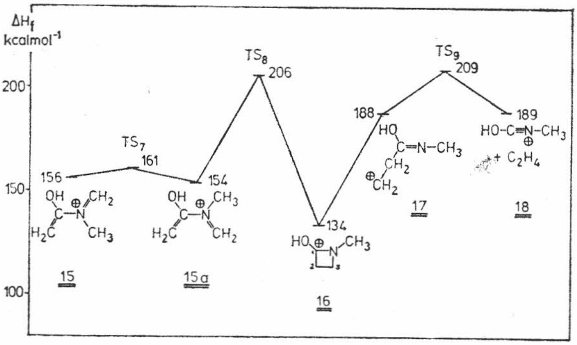
$$(Me)_2N-C(=O)CH_2X^{+\cdot} \longrightarrow C_4H_8NO^+ + X^{\cdot} \qquad (2)$$

X = Cl , NO_2

Reaction (2) has been studied only by MNDO. The most important points of the potential energy hyperface are shown in scheme 2 for $X = Cl$. The energy profile presented here is typical insofar as the simple bond breaking via TS_{10} leading to the rearranged structure **13** is energetically unfavourable and instead of this dissociation is preceeded by H-shift yielding structure **14** which has a much lower activation barrier for dissociation. Scheme 2(b) shows the rather comlicated sequence of rearrangements leading to $HO—C=N—CH_3^+$ and C_2H_4 as final products of the reaction. The proposed mechanism explains the complete hydrogen scrambling which was found experimentally by isotope labelling because structure **16** allows 1,2 H-shifts along the ring and the hydroxyl hydrogen. Structure **16** is also the global minimum on the $C_4H_8NO^+$ energy hyperface which was supported by 4-31G calculations.[5b]







CONCLUSIONS

The combination of elaborate experimental techniques and SCF calculations provide valuable information on the energetics and stereochemistry of reaction pathes which shift the degree of assumptions on chemical reactions a bit more towards knowledge. A lot of problems being unsolved can be tackled by methods already available. The development of modern computers making more reliable calculations possible will facilitate this process even further.

Acknowledgments. — Some of the calculations have been performed by the group of Dr. Y Apeloig, Haifa, Israel, whose cooperation is gratefully acknowledged. Financial support is given by the Deutsche Forschungsgemeinschaft (Schw 221/6/2) and the Fonds der Chemischen Industrie (Liebig-Scholarship to G. F.).

REFERENCES

1. M. J. S. Dewar and W. Thiel, *J. Amer. Chem. Soc.* **99** (1977) 4899.
2. a) I. W. McIver, Jr and A. Komornicki, *J. Amer. Chem. Soc.* **94** (1972) 2625; b) D. Poppinger, *Chem. Phys. Lett.* **34** (1975) 332.
3. Quantum Chemistry Program Exchange, Bloomington, Indiana, program 368.
4. Y. Apeloig, B. Ciommer, G. Frenking, M. Karni, A. Mandelbaum, H. Schwarz, and A. Weisz, *J. Amer. Chem. Soc.*, in press.
5. a) B. Ciommer, G. Frenking, and H. Schwarz, *Chem. Ber.* **114** (1981) 1503; b) G. Frenking and H. Schwarz, *J. Comp. Chem.* **3** (1982) 251.
6. G. Frenking, S. Meyn, and H. Schwarz, in preparation for publ.

SAŽETAK

SCF-proračuni kao sredstva za interpretaciju reakcijskih mehanizama — slučajevi otpuštanja CO_2 iz ioniziranog $ClCH_2$—$COOCH_3$ i C_2H_4 iz ioniziranog $(CH_3)_2N$—$COCH_2X$

G. Frenking i H. Schwarz

Lokalizacija prijelaznih stanja kao prijevojnih točaka koje imaju jednu negativnu vlastitu vrijednost u matrici konstanti sila daje važne informacije o energijskim hiperpovršinama kemijskih reakcija. Ona se može upotrijebiti za određivanje reakcijskih mehanizama kod neobičnih eksperimentalnih rezultata i demonstrirana je kao takva u reakcijama iz naslova.