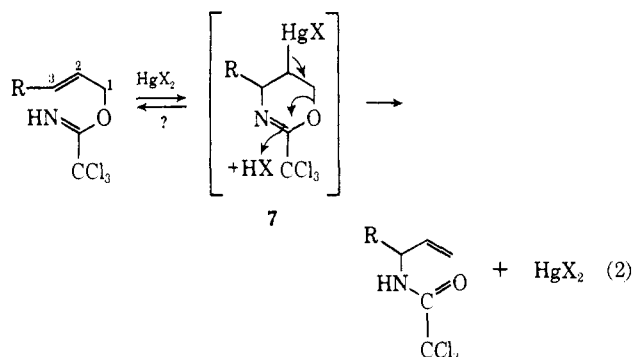


observed at -78° ,⁹ and a second double bond does not interfere as compound **6** can be obtained in 79% isolated yield. Catalysis is not observed with all the trichloroacetimidates studied and is most successful for derivatives of 3-substituted primary allylic alcohols (Table I).

Mercuric ion catalysis of a formal [3,3]-sigmatropic rearrangement is to our knowledge unprecedented. A two-step mechanism involving iminomercuration-deoxymercuration is proposed. In the first step the mercuric electrophile adds to the carbon-carbon double bond to form a mercurinium ion (or its equivalent)¹¹ which is then captured intramolecularly at C-3 by the nucleophilic imino nitrogen to afford **7**.^{12,13} Intermediate **7** can then suffer cleavage of the carbon-oxygen bond (deoxymercuration)¹⁴ to afford the rearranged amide product. The success of this catalyzed reaction derives from the fact that in aprotic solvents adduct formation between an olefin and mercuric trifluoroacetate is both rapid and reversible,¹⁵ a feature which we have utilized previously.¹⁶ Evidence for the mechanism of eq 2 derives mainly from the observed de-



pendence of the catalyzed reaction on trichloroacetimidate structure. Thus the catalyzed reaction is successful for imidates with R groups which promote nucleophilic addition to C-3 and fails in cases such as allyl, 1-hepten-3-yl, and 2-cyclohexen-1-yl¹⁶ where nucleophilic addition at C-2 is favored.¹⁷ Consistent also with this mechanism is the failure of mercuric trifluoroacetate (or mercuric acetate) to catalyze the rearrangement of **5** in protic solvents such as methanol, and the failure of stronger Lewis acids such as aluminum chloride etherate,¹⁸ silver fluoroborate,¹⁸ or boron trifluoride etherate^{6,2d} to promote this rearrangement.

(9) The catalyst was destroyed by reduction¹⁰ at -78° before workup.

(10) H. C. Brown, P. J. Geoghegan, Jr., G. L. Lynch, and J. T. Kurek, *J. Org. Chem.*, **37**, 1941 (1972).

(11) Cf. G. A. Olah and P. R. Clifford, *J. Amer. Chem. Soc.*, **95**, 6067 (1973), and references cited therein.

(12) Although aminomercuration reactions are well known,¹³ there are, to our knowledge, no previous reports of iminomercuration. Iminomercuration has, however, been observed in other unpublished work in our laboratory.¹⁷

(13) Cf. H. K. Hall, Jr., J. P. Schaefer, and R. J. Spangord, *J. Org. Chem.*, **37**, 3069 (1972), and references cited therein.

(14) M. M. Kreevoy and M. A. Turner, *J. Org. Chem.*, **30**, 373 (1965), and other papers in this series.

(15) (a) H. C. Brown and M.-H. Rei, *J. Chem. Soc. D*, 1296 (1969); (b) H. C. Brown, M.-H. Rei, and K.-T. Liu, *J. Amer. Chem. Soc.*, **92**, 1760 (1970).

(16) L. Overman, *J. Chem. Soc., Chem. Commun.*, 1196 (1972).

(17) In these cases the use of 1 equiv of mercuric trifluoroacetate results in ring closure by the addition of the imino nitrogen atom at C-2. Subsequent transformation of these intermediates affords the corresponding 2-amino alcohols; details to be reported in a future publication.

(18) Such treatment in THF results in the disappearance of **3** without formation of any detectable **4**. Details of this conversion will be reported in a future publication.

The 1,3 transposition of the $-OH$ and $-NH_2$ groups reported here will likely be most useful in the synthesis of highly hindered amines (or amides), e.g., **6** and **8**, for which there are few alternate methods.¹⁹ The ease of hydrolytic removal of the trichloroacetyl group²⁰ and the low temperature of the catalyzed conversion are two important features of the overall transformation.

The following procedure for the catalyzed reaction is representative. Geranyl trichloroacetimidate **5** (25 mmol, prepared in 92% yield from geraniol) was dissolved in 125 ml of THF and cooled to -78° under nitrogen. A solution of mercuric trifluoroacetate²¹ (25 ml of a 0.2 M THF solution) was added dropwise over 15 min. The resulting solution was allowed to warm to room temperature during 1 hr, and pyridine (8 ml) was added to complex free mercuric ion.^{15a} THF and excess pyridine were removed *in vacuo*, ether was added, and the ether solution was washed with H_2O until the aqueous extracts gave a negative test for ionic mercury ($NaBH_4-NaOH$).¹⁰ Drying ($MgSO_4$) and short-path distillation afforded 5.93 g (79%) of **6**: bp $111-114^\circ$ (0.5 Torr); ν_{max} 1700 (C=O) and 3420 cm^{-1} (N-H); τ (CCl_4) 3.41 (broad singlet, 1 H, O=CNH); 3.8-5.2 (multiplet, 4 H, =C-H), 8.33, 8.41, and 8.52 (singlets, 3 H each, CH_3).

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-38634X) and the Merck Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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Larry E. Overman

Department of Chemistry, University of California, Irvine
Irvine, California 92664

Received September 4, 1973

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XX. $C_3H_7^+$ Cations with a Polarized Basis Set

Sir:

The structure of protonated cyclopropane and of the $C_3H_7^+$ potential energy surface remains a problem intensively investigated by both experimental¹⁻³ and theoretical^{4,5} means. Our previous study of the $C_3H_7^+$

(1) M. Saunders, P. Vogel, E. L. Hagan, and J. Rosenfeld, *Accounts Chem. Res.*, **6**, 53 (1973) and references cited therein. Also see D. M. Brouwer and H. Hogeveen, *Progr. Phys. Org. Chem.*, **9**, 179 (1972).

(2) S.-L. Chong and J. L. Franklin, *J. Amer. Chem. Soc.*, **94**, 6347 (1972).

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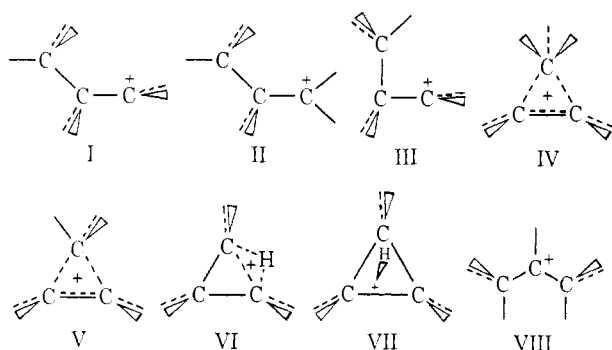
(5) (a) MINDO/2 has been applied to the $C_3H_7^+$ surface, but the results are in poor agreement with experiment (N. Bodor and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **93**, 6686 (1971); N. Bodor, M. J. S. Dewar, and D. H. Lo, *ibid.*, **94**, 5303 (1972); M. J. S. Dewar, XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., Vol. 1, July 1971, Butterworths, London, p 1). (b) A MINDO/3 study gives more reasonable results (M. J. S. Dewar, Abstracts, 23rd National Organic Chemistry Symposium of the American Chemical Society, Tallahassee, Fla., June 1973, p 26.)

Table I. Energies of C₃H₇⁺ Structures

Cation	Total energy (hartrees)			Relative energy (kcal mol ⁻¹)		
	STO-3G	4-31G	6-31G*	STO-3G	4-31G	6-31G*
2-Propyl (VIII)	-116.02765	-117.20864	-117.37749	0	0	0
Corner-protonated cyclopropane (IV)	-115.99130	-117.18109	-117.35681	22.8	17.3	13.0
Corner-protonated cyclopropane (V)	-115.99117	-117.18091	-117.35665	22.9	17.4	13.1
Methyl-eclipsed 1-propyl (III)	-115.99500	-117.18167	-117.35504	20.5	16.9	14.1
Methyl-staggered 1-propyl (I)	-115.99631	-117.18092	-117.35043	19.7	17.4	17.0
Methyl-staggered 1-propyl (II)	-115.99416	-117.17776	-117.34752	21.0	19.4	18.8
Edge-protonated cyclopropane (VI)	-115.98450	-117.16541	-117.34713	27.1	27.1	19.1
Face-protonated cyclopropane (VII)	-115.77102	-116.98612	-117.17013	161.0	139.6	130.1

potential surface using *ab initio* molecular orbital theory employed optimized geometries (with prescribed symmetry constraints) using the minimal STO-3G basis set.⁶ Single computations were then carried out using the extended (split-valence) basis 4-31G⁷ and certain predictions about the true potential surface were made from the corresponding energies. Since this work was completed, it has become evident that relative energies of hydrocarbons and other molecules, particularly the relative stability of open and cyclic structures, are significantly altered by the addition of polarization functions to the basis.^{8,9} It is therefore important to re-examine our conclusions at a more accurate level. In this note we report new energies (at the same previously reported geometries⁴) using the 6-31G* basis which includes d functions on carbon.¹⁰

The structures examined are I-VIII. The calculated



total energies and energies relative to the most stable form are listed in Table I, along with the previous 4-31G and STO-3G energies. There are some significant changes in the relative ordering. The following points should be noted.

(1) The theory still predicts that 2-propyl VIII is the most stable form of C₃H₇⁺, a conclusion which is common to all the basis sets used in *ab initio* molecular orbital treatments.

(2) The second most stable structure is now found to be the corner-protonated cyclopropane IV. This has an energy almost identical with its conformational

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(8) (a) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972); (b) P. C. Hariharan and J. A. Pople, *ibid.*, **16**, 217 (1972). (c) A very recent paper [B. Zurawski, R. Ahlrichs, and W. L. Kutzelnigg, *Chem. Phys. Lett.*, **21**, 309 (1973)] suggests that the bridged form of the ethyl cation is further stabilized relative to the classical form when correlation effects are taken into account.

(9) (a) A. Rauk, L. C. Allen and E. Clementi, *J. Chem. Phys.*, **52**, 4133 (1970); (b) R. M. Stevens, *ibid.*, **55**, 1725 (1971).

(10) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, **28**, 213 (1973).

isomer, V, indicating nearly free rotation of the methyl group. With the previous 4-31G calculations, IV was found to be very slightly (0.4 kcal mol⁻¹) less stable than the asymmetric methyl-eclipsed structure III which can be considered as a distortion of V. However, it has become clear^{8,9} that the addition of carbon d functions to the basis preferentially lowers the energy of three-membered rings, so that it is not surprising that IV and V now become more stable than III. Although it is not completely demonstrated by the limited number of computations performed, it does seem likely that IV or V are close to a local minimum on the 6-31G* surface, indicating that corner-protonated cyclopropane is a second isomer of C₃H₇⁺.

(3) The new results indicate that the 1-propyl structures with staggered arrangements for the C₂-C₃ bonds (I and II) are 4-6 kcal mol⁻¹ less stable than corner-protonated cyclopropane. Rotation about the C₁-C₂ bond gives lowest energy (I) with C₂-C₃ oriented so as to hyperconjugate most effectively with the carbonium center. This was found previously.⁴ However, it is not yet clear whether I is close to a local minimum in the surface or whether the potential surface goes directly down with methyl motion to the corner protonated cyclopropane V.

(4) Addition of carbon d functions lowers the energy of edge-protonated cyclopropane VI substantially and the gap between this form and the corner-protonated IV is reduced to 6 kcal mol⁻¹. The previous computations indicated that the edge-protonated form VI was only a transition state on the surface and not a metastable intermediate. There is no apparent reason to change this conclusion.

(5) Since the addition of polarization d functions on carbon modified some of the theoretical predictions, it is pertinent to inquire whether addition of p functions on hydrogen¹⁰ would lead to further changes. Such computations on C₃H₇⁺ are beyond our capacity at present, but we may note that computations with such a basis (6-31G**) on smaller systems¹⁰ indicated that the energy lowering on addition of p functions per hydrogen atom in C-H bonds was fairly constant at about 1 kcal mol⁻¹. The only exception was a bridging hydrogen position where the lowering was 2-3 kcal mol⁻¹. Thus it seems possible that edge-protonated cyclopropane VI may be further stabilized relatively at this higher level of theory leading to an energy only 4-5 kcal mol⁻¹ above the corner-protonated form IV.

(6) We have not been able to obtain a 6-31G* energy for the H-bridged propyl cation, which is intermediate between the 1-propyl and 2-propyl cations. This was investigated at the 4-31G level previously.⁴ However, experience with the ethyl cation surfaces⁸ indicates

that the 4-31G \rightarrow 6-31G* energy lowering is about 7 kcal mol⁻¹ greater for the bridged form than for the classical form. This suggests that the energy of the H-bridged form at the 6-31G* level is about 11 kcal mol⁻¹ relative to 2-propyl, so that there may be a direct descent without activation from I to VIII.

Recent ion cyclotron resonance studies by McAdoo, McLafferty, and Bente³ suggest that the most stable form of C₃H₇⁺ is 2-propyl and that protonated cyclopropane either isomerizes to the 2-propyl cation or is higher in energy than the latter by *ca.* 7 kcal mol⁻¹. Similar conclusions have been reached by Chong and Franklin² on the basis of measurements of gas-phase ionic equilibrium constants. They demonstrated the existence of a second isomeric species of C₃H₇⁺ about 9 kcal mol⁻¹ less stable than the 2-propyl cation and identified this with protonated cyclopropane. According to our theoretical study, this is the corner-protonated form IV or V (with a theoretical energy of 13 kcal mol⁻¹ relative to 2-propyl). Lossing and Semeluk¹¹ obtain a heat of formation for the 1-propyl cation which is 16 kcal mol⁻¹ above that for the 2-propyl cation. This is obtained from the ionization potential of the 1-propyl radical and corresponds well with our relative energy of 17 kcal mol⁻¹ for structure I. However, it should be emphasized that I may not be a separate isomer and may rearrange directly to the corner-protonated form IV or V or to VIII. Finally, we may note that our results are consistent with the nuclear magnetic resonance data in superacid systems.¹ Saunders, *et al.*,¹ conclude that hydrogen and carbon scrambling in protonated cyclopropanes can best be interpreted in terms of a corner-protonated transition state. The lower energy barrier to 1,3-hydride shifts (now 6 kcal mol⁻¹ or less) is more consistent with experimental results on corner-to-corner hydrogen migration than the previous 4-31G barrier.⁴

Acknowledgments. This work was supported by National Science Foundation Grants GP-25617 and GP-29078X and at Princeton by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Hoffmann-La Roche Inc., Nutley, N. J.

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P. C. Hariharan, L. Radom, J. A. Pople*

Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

P. v. R. Schleyer

Department of Chemistry, Princeton University
Princeton, New Jersey 08540

Received September 1, 1973

Photochemical Reaction Pathways of Ruthenium(II) Complexes. Evidence Regarding the Reactive Excited State(s) from Metal-to-Ligand Charge Transfer Excitation of Ru(NH₃)₅py²⁺ and Related Complexes

Sir:

Some strikingly contrasting photochemical behavior results from the irradiation of metal-to-ligand charge transfer (MLCT) absorption bands of ruthenium(II) complexes of nitrogen heterocycle ligands. In ambient

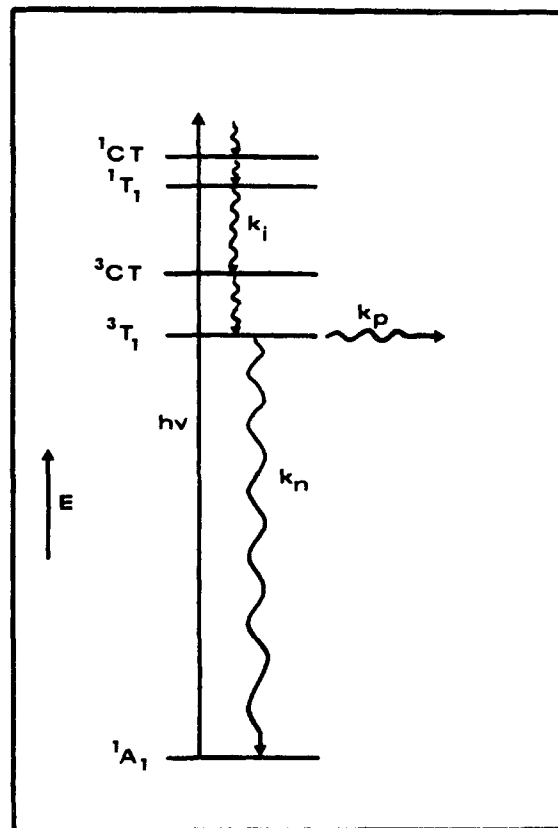


Figure 1. Excited-state diagram for the proposed mechanism for photoaquation of Ru(NH₃)₅py²⁺; *k_p* represents reactions leading to photoproducts.

temperature fluid solution, the ions Ru(bipy)₃²⁺ and *cis*-Ru(bipy)₂(4-stilbazole)₂²⁺ are both essentially inert toward substitution, but the former ion displays significant phosphorescent emission¹ while MLCT excitation of the latter ion leads to very weak phosphorescence and primarily to *cis/trans* isomerization of the 4-stilbazole ligand.² A third behavior is observed with aqueous Ru(NH₃)₅py²⁺ where MLCT excitation results almost exclusively in substitution reactions.^{3,4} Substitutional behavior is not intuitively expected for the MLCT excited state⁴ of Ru(NH₃)₅py²⁺ given that Ru(III) amine complexes are relatively substitution inert.⁵ Thus, it has been argued⁴ that the substitution reactive state is ligand field in character, perhaps the triplet ³T₁. As charge transfer and ligand π-π* absorptions dominate the spectrum, the presence of such a state can only be inferred. Here, we present photochemical evidence that MLCT excited states are relatively unreactive toward substitution and that another, presumably ligand field, excited state is responsible for the photosubstitution reactions of Ru(NH₃)₅py²⁺.

Figure 1 is a simplified excited-state diagram for the proposed mechanism.⁴ Initial excitation is assumed to be followed by efficient intersystem crossing-internal

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