Ground States of σ-Bonded Molecules. II.[1] Strain Energies of Cyclopropanes and Cyclopropenes[2]

N. Colin Baird[3] and Michael J. S. Dewar

Contribution from the Department of Chemistry, The University of Texas, Austin, Texas 78712. *Received March 13, 1967*

Abstract: The SCF MO procedure described in part I[1] has been applied to a wide range of strained microcyclic compounds containing three-membered rings. The results agree well with available experimental data, indicating that this procedure automatically provides estimates of the effect of ring strain in molecules of this type. Several surprising predictions follow from these calculations, notably that tetrahedrane should not exist as a stable species, except perhaps in matrices at low temperatures, whereas bicyclobutadiene should be thermally stable.

The ultimate goal of the program described in this series of papers is to develop a general quantitative treatment of the geometries and heats of atomization of molecules and transition states. A few years ago such an endeavor would have seemed ridiculously optimistic; however, recent work[4] has shown that the heats of atomization and geometries of conjugated molecules can be calculated with quite unexpected accuracy by a variant of the Pople SCF MO method, using the Hückel $\sigma-\pi$ approximation and treating the σ bonds as localized, so it no longer seems at all unreasonable to hope that the more general problem might likewise be solved by some appropriate version of this kind of approach.

In part I, we described an appropriate modification of the Pople method in which all the valence electrons in a molecule are included; this approach was shown to give satisfactory estimates of the heats of atomization of a number of hydrocarbons, including paraffins, olefins, and benzene. Previous attempts to carry out calculations of this kind had either been limited to diatomic molecules[5] or had been carried out with the object of reproducing the results that would be given by an *a priori* Hartree–Fock treatment;[6,7] calculations of this kind cannot of course give satisfactory estimates of heats of atomization, since the Hartree–Fock method is known to be far too inaccurate for this purpose. The heats of formation reported in these investigations differed from the experimental values by large factors. Our approach differed from them in that the parameters were chosen to give good estimates of heats of atomization, rather than to reproduce the results of a Hartree–Fock calculation.

The results obtained in part I were admittedly far from ideal in several respects, and the particular approach used there should be regarded as preliminary in nature. Nevertheless, we decided to extend it to other types of hydrocarbons for three reasons. Firstly, we wished to see if the method would give reasonable estimates of strain energies in cyclic systems; previous calculations, in particular those based on the extended Hückel method,[8] had proved unsatisfactory in this respect. Secondly, if the method proved satisfactory for such compounds, it seemed likely to lead to useful predictions in a very active and topical area of organic chemistry. Thirdly, we hoped that such calculations might throw light on the importance of $\sigma-\pi$ interactions in conjugated systems. Here we report the first part of this investigation, a study of various derivatives of cyclopropane and cyclopropene.

Procedure

The calculations followed the pattern described in part I using the same parameters. The heat of atomization of a molecule is found from the calculated total energy by subtracting a sum of the energies of appropriate barycenters of the constituent atoms. Ideally, the calculations should refer to heats of atomization of molecules in their equilibrium configurations, *i.e.*, without any vibrational energy; since such equilibrium heats of atomization cannot as a rule be estimated from available experimental data, we chose the parameters in our treatment to reproduce standard heats of formation at 25°. The assumptions underlying this kind of approach are well known and need not be repeated here.

One quantity of especial interest in the case of small-ring compounds is the strain energy, *i.e.*, the difference in energy between the compounds and the value that would be expected for a strain-free analog. In order to estimate strain energies, one must therefore be able to estimate the heats of atomization of strain-free analogs. To do this, we used Franklin's group method and the group values calculated by him.[9]

In order to apply our SCF MO method, it is necessary to know the geometries of molecules. Since accurate structures are available only in a few cases, we deduced the geometries from the following assumptions: (a) bond lengths have the "standard" values assumed in part I and listed in Table I; these are close to the average bond lengths in "Interatomic Distances";[10] (b) saturated carbon atoms have tetrahedral geometry,

---

[1] Part I: M. J. S. Dewar and G. Klopman, *J. Am. Chem. Soc.*, **89**, 3089 (1967).

[2] This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.

[3] Robert A. Welch Postdoctoral Fellow.

[4] A. L.-H. Chung and M. J. S. Dewar, *J. Chem. Phys.*, **42**, 756 (1965); M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, **87**, 685, 692, 3255 (1965); **88**, 1349 (1966); *Tetrahedron*, 21, 1817, 3423 (1965); *J. Chem. Phys.*, **44**, 759 (1966); *Tetrahedron Letters*, **50**, 4503 (1965); M. J. S. Dewar and C. C. Thompson, Jr., *J. Am. Chem. Soc.*, **87**, 4414 (1965).

[5] G. Klopman, *ibid.*, **86**, 4550 (1964).

[6] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965); **44**, 3289 (1966).

[7] M. D. Newton, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **88**, 2353, 2361, 2367 (1966).

[8] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).

[9] J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

[10] L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965.

Table I. Standard Bond Lengths

Bond	Hybridization[a]	Length, nm
C—C	te–te	0.1534
	te–tr	0.1520
	tr–tr	0.1483
C=C		0.1337
C—H	te	0.1093
	tr	0.1083

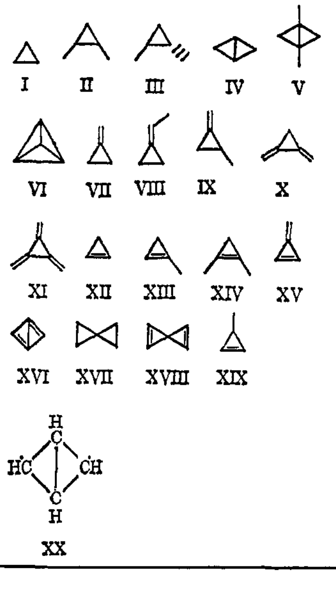
[a] te = tetrahedral; tr = trigonal.

except those in small rings; (c) bond angles about the olefinic carbon atoms in the groups $=CH_2$ and $=CH-CH_3$ are 120°; (d) the exocyclic bond angle at a saturated carbon atom in three-membered cyclopropane or cyclopropene is 120°; (e) exocyclic atoms or groups bisect the CCC angle between carbon atoms in the ring; (f) the dihedral angle for bridgehead carbon atoms in nonplanar bicyclic systems in 121°; (g) conformations of methyl groups are chosen to minimize the total energy.

Results and Discussion

In Table II the skeletal structures of compounds I–XX are shown. Table III shows heats of atomization calculated for various derivatives of cyclopropane and cyclopropene, together with experimental values where these are available. The final columns show strain energies estimated by the method indicated in the previous section.

Table II

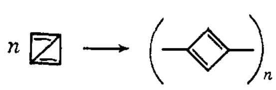


The agreement between the calculated and observed heats of atomization is surprisingly good, considering the inevitable uncertainties in the assumed geometries. Evidently our procedure automatically leads to good estimates of strain energies in these microcyclic systems, in contrast to the extended Hückel method. Only in one case (spiropentane) is the error greater than 7 kcal/mole.

The results for tetrahedrane (VI) and bicyclobutadiene (XVI) are of especial interest. Tetrahedrane is predicted to have an extremely large strain energy, greater by 83 kcal/mole than that of bicyclobutane. Since this is approximately the same as the bond energy of a carbon–carbon single bond, the conversion of VI to the bicyclobutadiene biradical (XX) should be almost thermoneutral. If this is so, tetrahedrane must be unable to exist as a stable entity, since it would immediately isomerize *via* XX to cyclobutadiene. Even if our calculated heat of atomization for VI is in error by as much as 20 kcal/mole, which seems most unlikely judging by the results for the other compounds listed in Table III, VI would not be isolable at room temperature, its predicted lifetime even at −40° being of the order of 10 sec. Substituted tetrahedranes should be even less stable, since any substituent would facilitate the conversion of VI to the biradical XX. The only hope of preparing compounds of this type seems to lie in the photochemical production of VI itself in a matrix at low temperature.

On the other hand, our calculations suggest that the unlikely looking molecule bicyclo[1.1.0]butadiene (XVI) should be thermally stable, having moreover a heat of atomization much greater than that (676 kcal/mole) estimated[11] for the isomeric diacetylene, HC≡CC≡CH. Calculations are listed in Table III for several configurations of XVI: (a) a planar classical structure (XVIa) with two "classical" double bonds (length, 1.337 A) and three classical single bonds (length, 1.483 A); (b) a bent molecule (XVIb) with the same bond lengths, but with an interannular dihedral angle of 121°; (c) a planar rhombic molecule (XVIc) with all bond lengths equal (1.41 A); (d) a square-planar molecule (XVId) with sides of 1.41 A. The planar classical model (XVIa) is predicted to be the best, being more stable by 2 kcal/mole than the bent form (XVIb), by 6 kcal/mole than the planar rhombic form (XVIc), and by 77 kcal/mole than the square form (XVId). The strain energy calculated for XVIa is actually *less* than twice that of cyclopropene!

Our calculations therefore lead to the amusing and very unexpected prediction that it should be impossible to make the reasonable-looking tetrahedrane (VI), at any rate at normal temperatures, but feasible to make bicyclobutadiene (XVI). If so, it might be possible to obtain XVI by photochemical cyclization of diacetylene in a matrix; it should of course be an extremely reactive species, polymerization to polycyclobutadiene being predicted to be exothermic, *i.e.*



$\Delta H = -41n$ kcal/mole. This value is about twice the heat of polymerization of vinyl derivatives.

The values listed in Table III suggest that there are relatively large steric interactions between pairs of methyl groups *cis* to one another in cyclopropane. Thus the strain energy calculated for *cis*-1,2-dimethylcyclopropane (II) is greater by 5.7 kcal/mole than that of cyclopropane itself, a difference presumably due solely to mutual repulsion of the methyl groups. The corresponding difference between 1,2-dimethylcyclopropene (XIV) and cyclopropene (XII) is much smaller

---

[11] Calculated from the heat of formation for diacetylene estimated by M. Cowperthwaite and S. H. Bauer, *J. Chem. Phys.*, **36**, 1743 (1962).

Table III. Energies (kcal/mole) of Compounds Containing Three-Membered Rings

Molecule	Heat of atomization (calcd)	ΔH_f Calcd	ΔH_f Exptl	Error	Strain energy Calcd	Strain energy Exptl
Cyclopropane (I)	809.1	+16.2	+12.72[a]	3.5	31.0	27.5
cis-1,2-Dimethylcyclopropane (II)	1365.1	+10.4			36.7	
trans-1,2-Dimethylcyclopropane (III)	1367.7	+7.8			34.1	
Bicyclo[1.1.0]butane (IV)	940.8	+55.4			67.4	
1,3-Dimethylbicyclo[1.1.0]butane (V)	1500.2	+46.2	+39.7[b]	6.5	69.3	62.8
Tetrahedrane (VI)	745.9	+146.1			150.5	
Methylenecyclopropane (VII)	946.8	+49.4			42.4	
Ethylidenecyclopropane (VIII)	1228.3	+43.0	+36.1[b]	6.9	42.8	37.2
2-Methylmethylenecyclopropane (IX)	1226.3	+45.0	+39.4[b]	5.6	44.2	
Dimethylenecyclopropane (X)	1094.8	+72.3			45.9	
Trimethylenecyclopropane (XI)	1245.7	+92.3			49.2	
Cyclopropene (XII)	659.6	+61.5	+66.6[a]	5.1	47.5	52.6
1-Methylcyclopropene (XIII)	940.8	+55.4			50.3	
1,2-Dimethylcyclopropene (XIV)	1221.7	+49.6	+46.4[b]	3.2	50.2	47.0
Methylenecyclopropene (XV)	812.9	+79.1			58.1	
Bicyclo[1.1.0]butadiene (XVIa)	690.3	+97.5			82.3	
Bicyclo[1.1.0]butadiene (XVIb)	688.5	+99.3				
Bicyclo[1.1.0]butadiene (XVIc)	684.4	+103.4				
Bicyclo[1.1.0]butadiene (XVId)	613.1	+174.7				
Spiropentane (XVII)	1213.3	+58.0	+44.23[c]	13.8	75.2	61.4
Spiropentadiene (XVIII)	912.8	+150.1			109.8	
3-Methylcyclopropene (XIX)	939.1	+57.1			49.4	

[a] H. A. Skinner and G. Pilcher, *Quart. Rev.* (London), **20**, 264 (1966). [b] Personal communication from Professors W. von E. Doering and R. B. Turner. [c] F. M. Fraser and E. J. Prosen, *J. Res. Natl. Bur. Std.*, **54**, 143 (1955).

(2.7 kcal/mole), because the methyl groups are further apart in XIV than in II. The heats of hydrogenation of XII and XIV should therefore show a much greater difference than that generally observed (1.5–2 kcal/mole) between a *cis*-dialkylethylene and a tetraalkylethylene (*e.g.*, *cis*-2-butene and tetramethylethylene); the heats of atomization listed in Table III lead to the prediction that the heat of hydrogenation of XIV should be less than that of XII by 6.1 kcal/mole. Doering and Turner[12] have recently observed such a large difference between the two heats of hydrogenation, their measured value (8.8 kcal/mole) being even greater than our calculated one.

This interpretation is also supported by the similar strain energies calculated for bicyclobutane (IV) and its 1,3-dimethyl derivative (V).[13] The distance between the methyl groups is considerably greater in V than it is in *cis*-dimethylcyclopropane (II).

The calculated heats of atomization of methylenecyclopropane (946.8 kcal/mole) and 1-methylcyclopropene (940.8 kcal/mole) indicate that in this series the isomers with exocyclic double bonds should be the most stable; the same conclusion follows from a comparison of IX with XIV. Experimental data for these compounds are as yet lacking. Our calculations for the corresponding cyclobutenes and cyclopentenes[15] indicate that there the isomers with double bonds in the ring should be the more stable, in agreement with experiment.

The results for 1- (940.8 kcal/mole) and 3- (939.1 kcal/mole) methylcyclopropene are also of interest. The difference between their calculated heats of atomization is almost exactly that expected for an analogous pair of open-chain isomers, implying that the stabilization associated with attachment of methyl to unsaturated carbon is the same in both cases.

Our calculations also lead to the prediction that the strain energies of bicyclobutane (IV) and spiropentane (XVII) should be more than double that of cyclopropane; this is in agreement with experiment, although our calculated values are too high. We also predict that spiropentadiene (XVIII) should be a stable species, its strain energy exceeding twice that of cyclopropene by about the same amount that the strain energy of XVII exceeds twice that of cyclopropane.

Another interesting prediction is provided by the calculated heats of atomization of mono-, di-, and trimethylenecyclopropane (VII, X, and XI). Methylenecyclopropane is predicted to have a strain energy 11.4 kcal/mole greater than that of cyclopropane, but the increase in strain when adding a second and third unsaturated carbon atom into the ring is much less (about 3.5 kcal/mole in both cases). This is surprising, since the effects of *I* strain would be expected to increase uniformly along the series with the increasing number of unsaturated carbon atoms in the ring. Since trimethylenecyclopropane has now been synthesized,[16] this prediction should soon be open to experimental test.

Table IV shows net atomic charges for compounds I–XIX, and Table V lists net charges and mobile bond orders for the π electrons in those molecules containing unsaturated carbon atoms.

Analysis of these electron-density distributions lead to the following generalizations.

(1) The total electron densities of the saturated carbon atoms are close to those found for the alkanes, and follow the same order: $C_{\text{quaternary}} > C_{\text{tertiary}} > C_{\text{secondary}} > C_{\text{primary}}$. Bridgehead carbon atoms collect

---

[12] Personal communication from Professors W. von E. Doering and R. B. Turner.

[13] The strain energy quoted for V differs from that quoted by Turner, Goebel, Doering, and Coburn[14] because, in using Franklin's[9] method, they apparently omitted a correction for the presence of two adjacent quaternary carbon atoms. Inclusion of this correction alters the "unstrained" heat of formation by 5.4 kcal/mole.

[14] R. B. Turner, P. Goebel, W. von E. Doering, and J. F. Coburn, Jr., *Tetrahedron Letters*, **15**, 997 (1965).

[15] These will be reported in the following papers of this series.

[16] E. Dorko, *J. Am. Chem. Soc.*, **87**, 5518 (1965); P. A. Waitkus, L. I. Peterson, and G. W. Griffin, *ibid.*, **88**, 181 (1966).

Table IV. Net Charges for Atoms

Molecule	Ring H^a	Ring H^b	*exo*^{c} H	Ring C^d	Ring C^e	*exo*^{c} C
I	−0.028			+0.057		
II	−0.009 (H—C$_1$)		−0.059^f	−0.049 (C$_1$)		+0.223
	−0.036 (H—C$_3$)^f			+0.093 (C$_3$)		
III	−0.014 (H—C$_1$)		−0.066^f	−0.052 (C$_1$)		+0.253
	−0.035 (H—C$_3$)			+0.096 (C$_3$)		
IV	−0.037			+0.173		
	+0.014^g			−0.112^g		
V	−0.043^f		−0.075^f	+0.226		+0.312
				−0.226^g		
VI	+0.040			−0.040		
VII	−0.034		−0.026	+0.095	−0.110	+0.110
VIII	−0.033^f		−0.006 (H—C$_4$)	+0.088^f	−0.082	−0.012 (C$_4$)
			−0.063 (H—C$_5$)^f			+0.246 (C$_5$)
IX	−0.015 (H—C$_2$)		−0.024 (═CH$_2$)^f	−0.034 (C$_2$)	−0.088	+0.103 (═C)
	−0.037 (H—C$_3$)^f		−0.067 (—CH$_3$)^f	+0.108 (C$_3$)		+0.248 (—C)
X	−0.038		−0.028	+0.153	−0.080	+0.098
XI			−0.025		−0.032	+0.083
XII	−0.058	+0.036		+0.151	−0.054	
XIII	−0.063	+0.024	−0.063	+0.177	−0.178 (C$_1$)	+0.311
					−0.019 (C$_2$)	
XIV	−0.068		−0.063^f	+0.204	−0.144	+0.299
XV		+0.024	−0.021		+0.013 (C$_1$)	−0.014
					−0.002 (C$_2$, C$_3$)	
XVIa		+0.050			+0.015 (C$_1$)	
					−0.065 (C$_2$)	
XVII	−0.035			+0.118		
				−0.192^g		
XVIII		+0.009		+0.027	−0.015	
XIX	−0.035	+0.032	−0.067	+0.024	−0.036	+0.222

[a] Bound to a saturated carbon atom. [b] Bound to an unsaturated carbon atom. [c] *exo* = exocyclic. [d] Saturated carbon atom. [e] Unsaturated carbon atom. [f] Average value for atoms of the type in question. [g] Refers to a bridgehead bond or atom.

Table V. π-Orbital Net Charges and Bond Orders

Molecule	Ring C	Exocyclic C	Endocyclic π bond	Exocyclic π bond
VII	+0.091	−0.098		0.981
VIII	+0.101	−0.108		0.972
IX	+0.092	−0.099		0.980
X	+0.087	−0.090	0.193	0.970
XI	+0.080	−0.080	0.197	0.957
XII	+0.017		0.983	
XIII	+0.020 (C$_1$)		0.975	
	+0.010 (C$_2$)			
XIV	+0.014		0.966	
XV	+0.166 (C$_1$)	−0.288	0.266 (C$_1$–C$_3$)	0.912
	+0.061 (C$_2$, C$_3$)		0.939 (C$_2$–C$_3$)	
XVIa	+0.422 (C$_1$)		0.806 (C$_1$–C$_2$)	
	−0.422 (C$_3$)		0.368 (C$_1$–C$_3$)	
			0.193 (C$_1$–C$_4$)	
XVIII	+0.034		0.966	
XIX	+0.020		0.980	

more electron density than do the other saturated carbon atoms in the rings, which in turn are more negative than the carbon atoms of exocyclic methyl groups.

(2) The total electron densities of the hydrogen atoms decrease as the saturated carbon atom to which they are bonded is increasingly substituted.

(3) The electron density of a carbon atom increases as its unsaturation increases, and the electron density of the hydrogen atoms decrease as the carbon atom to which they are bonded increases in unsaturation. Both of these trends are in agreement with the population analyses for the open-chain hydrocarbons.

(4) With the exception of bicyclobutadiene (XVI), only one excited classical resonance structure can be drawn for the 1,3-dienes listed in Table III. For these systems, the π-electron bond orders of the classically "double" bonds are all very large (0.94 ± 0.04) and those of the classically "single" bonds are quite small (0.23 ± 0.04). These bond orders are comparable with those calculated for 1,3-butadiene (0.98 and 0.20), implying that the conjugation between the double bonds in these rings is of the same order of magnitude as that in 1,3-butadiene.

(5) In all the ring compounds having exocyclic double bonds, there is a pronounced tendency for the π electrons to migrate to the exocyclic carbon atom. This migration of π-electron density is counterbalanced by a migration of σ electrons in the opposite direction with the net result that the exocyclic carbon usually has a smaller total electron density than the unsaturated carbon atom in the ring.

(6) Although the total net charges of the carbon atoms in bicyclobutadiene are quite small, there are extensive migrations of the σ and π electrons between the carbon atoms. The σ charge migrates to the bridgehead carbon atoms, whereas the π charge migrates in the opposite direction, the latter trend being in agreement with Hückel calculations for this compound. The mobile bond order across the bridgehead carbon atoms (0.39) is substantially larger than that calculated for other "classically" single bonds.

Table VI lists calculated dipole moments for all except the symmetrical compounds (I, VI, XI, XVI, XVII, and XVIII) where of course the predicted moments are zero. Experimental values are available in only two cases and here the agreement with theory is only fair. Dipole moments should of course be particularly sensitive to the molecular geometry and hence badly affected by our enforced arbitrary choice of this in our calculations.

Table VI. Dipole Moments

Compound	Predicted dipole moment, D.	Exptl dipole moment, D.
cis-1,2-Dimethylcyclopropane (II)	0.15	
trans-1,2-Dimethylcyclopropane (III)	0.01	
Bicyclo[1.1.0]butane (IV)	0.35	0.68[a]
1,3-Dimethylbicyclo[1.1.0]butane (V)	0.34	
Methylenecyclopropane (VII)	0.18	
exo-Methylmethylenecyclopropene (VIII)	0.26	
2-Methylmethylenecyclopropane (IX)	0.18	
Dimethylenecyclopropane (X)	0.12	
Cyclopropene (XII)	0.27	0.45[b]
1-Methylcyclopropene (XIII)	0.41	
1,2-Dimethylcyclopropene (XIV)	0.45	
Methylenecyclopropene (XV)	0.87	
3-Methylcyclopropene (XIX)	0.34	

[a] M. D. Harmony and K. Cox, *J. Am. Chem. Soc.*, **88**, 5049 (1966). [b] P. H. Kasai, R. J. Meyers, D. F. Eggers, Jr., and K. B. Wiberg, *J. Chem. Phys.*, **30**, 512 (1959).

Table VII. Energy Levels (ev)

I	11.08, 13.16, 13.71, 15.85, 19.77
II	10.82, 10.85, 12.03, 12.45, 12.93, 13.24, 14.09, 14.17, 14.90, 15.83, 17.84, 19.32
III	10.80, 10.88, 12.07, 12.63, 13.15, 13.79, 14.09, 14.26, 14.46, 15.05, 18.61, 19.04
IV	10.39, 10.87, 11.67, 11.96, 13.60, 14.00, 15.45, 18.35, 18.79
V	10.21, 10.77, 11.03, 11.89, 12.54, 13.65, 13.75, 13.95, 14.33, 14.63, 15.21, 16.39, 17.78
VI	9.58, 11.72, 14.90, 18.68
VII	10.74, 10.81, 10.94, 13.03, 13.30, 14.46, 15.29, 17.13, 19.53
VIII	10.61, 10.69, 10.92, 13.03, 13.21, 14.26, 14.50, 15.31, 16.87, 19.51
IX	10.67, 10.76, 10.81, 12.39, 13.09, 13.80, 14.12, 14.48, 15.02, 17.02, 18.84
X	10.19, 10.57, 10.87, 11.27, 13.16, 14.20, 14.51, 14.61, 16.02, 18.17
XI	10.21, 10.57, 12.58, 13.06, 14.13, 14.42, 16.21
XII	10.32, 10.86, 11.38, 14.40, 14.42, 18.34, 19.66
XIII	10.18, 10.62, 11.13, 13.50, 14.02, 14.33, 14.66, 16.92, 19.42
XIV	10.06, 10.45, 10.88, 12.91, 13.95, 14.15, 14.18, 14.40, 14.80, 15.73, 18.68
XV	9.60, 10.69, 11.49, 12.28, 14.03, 14.06, 17.09, 18.64
XVIa	9.16, 11.09, 11.64, 12.51, 13.02, 16.73, 16.83
XVII	10.64, 10.68, 11.87, 13.12, 13.28, 13.76, 15.23, 17.13, 19.84
XVIII	9.58, 10.92, 12.10, 12.68, 14.76, 17.42, 18.44
XIX	10.24, 10.73, 11.28, 13.07, 13.65, 14.09, 14.88, 18.42, 18.55

In part I[1] it was shown that there is a remarkable correlation between the orbital energies calculated by our method and the ionization potentials measured by Al-Jaboury and Turner[17] by their novel photoelectron spectroscopic technique. The correlation held for all orbitals with binding energies up to 20 ev. No good data seem as yet to be available for any of the compounds discussed in this paper; the few values reported were obtained by electron impact and therefore both are numerically unreliable and also refer only to the first ionization potentials.[17] Undoubtedly photoelectron spectroscopic studies will soon become available for these materials; we have therefore listed our calculated orbital energies in Table VII, in the hope that they may assist in interpreting such measurements.

---

[17] M. I. Al-Jaboury and D. W. Turner, *J. Chem. Soc.*, 5141 (1963); 4434 (1964); 616 (1965).

Nuclear Magnetic Resonance Studies on Exchange Reactions of Group III Alkyl Derivatives. II

J. Barry DeRoos[1] and John P. Oliver

Contribution from Wayne State University, Detroit, Michigan 48202.

Received August 8, 1966

Abstract: The exchange of trimethylgallium with trimethylgallium–dimethylamine (I), trimethylgallium–monomethylamine (II), trimethylgallium–ammonia (III), and trimethylgallium–dimethyl ether (IV) addition compounds has been investigated. This exchange proceeds through a dissociation step for I, but has been shown to proceed by an electrophilic displacement reaction for II and III. Activation energies were determined to be 19, 10, and 8.5 kcal/mole, respectively, for I, II, and III. The reaction of IV was too fast to follow by the techniques available. An explanation for this drastic change in mechanism is given, and the results are compared with those observed for similar exchange reactions of boron trifluoride addition compounds.

There has been a rapidly expanding interest in the exchange reactions of group III addition compounds as cited previously.[2] Unfortunately, there is still considerable confusion regarding the mechanisms of molecular exchange in these systems. Brownstein, *et al.*,[3] present two possible mechanisms for exchange in BF_3–base systems: dissociation

$$\mathrm{AB} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{A} + \mathrm{B} \tag{1}$$

or bimolecular displacement

$$\mathrm{A}' + \mathrm{AB} \overset{k_1}{\rightleftharpoons} \mathrm{A}'\mathrm{B} + \mathrm{A} \tag{2}$$

Their data suggest that both mechanisms may be operative depending upon the base present, but it is difficult to establish any trends for the reported reactions be-

---

[1] Recipient of a NASA Traineeship for 1964–1966.

[2] J. B. DeRoos and J. P. Oliver, *Inorg. Chem.*, 4, 1741 (1965).

[3] S. Brownstein, A. M. Eastham, and G. A. Latremouille, *J. Phys. Chem.*, 67, 2020 (1963); S. Brownstein and J. Paasivirta, *J. Am. Chem. Soc.*, 87, 3593 (1965).