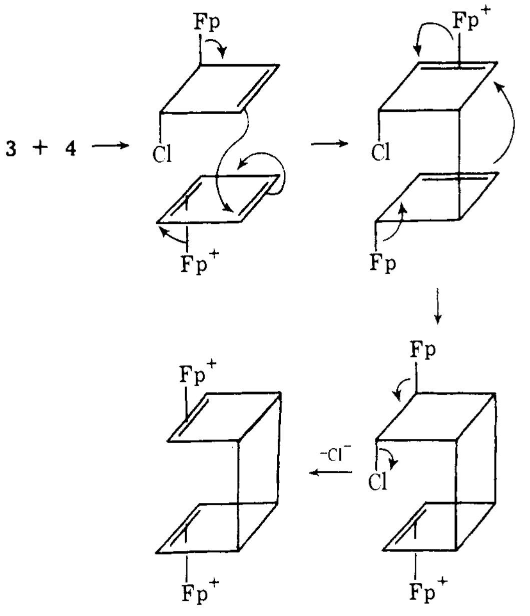
Scheme III



3 and 4 as outlined in Scheme III. It is interesting that the syn tricyclooctadiene is formed rather than the anti isomer which would have been predicted on steric considerations. This result suggests an attractive interaction between the chloro group of **4** and the electrophilic cyclobutadiene ring of **3**.

The aforementioned experiments demonstrate that there exists a class of cyclobutadiene transition metal complexes in which the cyclobutadiene ligand exhibits a degree of reactivity reminiscent of that attributed to free cyclobutadiene, and that the mode of reactivity of the η^2-cyclobutadiene ligand of **3** is somewhat altered as compared to cyclobutadiene in that the ligand is electrophilic and, in the Diels–Alder reaction, only functions as a dienophile. It is particularly important to note that the formation of *syn*-tricyclooctadiene can no longer be considered prima facie evidence for the intermediacy of free cyclobutadiene in reactions involving transition metals. Our results support the contention that transient cyclobutadiene complexes generated by the oxidative degradation of cyclobutadienetricarbonyliron are not involved in the formation of cyclobutadiene–dienophile adducts.[12-14] However, our results do suggest that η^2-cyclobutadiene complexes may indeed be involved in the formation of cyclobutadiene–diene adducts.

Acknowledgment. We gratefully acknowledge the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

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(3) The petroleum ether insoluble materials are binuclear complexes, which have been previously described.[2]
(4) The failure to observe a high field resonance (~τ 9.3) characteristic of Cp(CO)$_2$Fe(norboradiene)$^+$ and Cp(CO)$_2$Fe(norbornylene)$^+$ complexes indicates that the iron is bonded to the double bond of the four-membered ring. Furthermore the resonance of the olefinic protons of the four-membered ring in **6** is observed at higher field as compared to the analogous resonance in **7**. This is consistent with complexation of the four-membered ring. The resonance of the olefinic protons of the five-membered ring in **6** is observed at lower field than the analogous resonance in 7.
(5) Reductive demetalation by NaCp(CO)$_2$Fe of the olefin ligand in Cp-(CO)$_2$Fe(olefin)$^+$ is virtually instantaneous and quantitative. In contrast we have found the iodide displacement[6] of olefin ligands to be extremely slow in certain instances.
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(8) Because of the insolubility of 1,3-diphenylisobenzofuran in CH$_2$Cl$_2$ at −78° only a 2.5% yield of **8** was obtained. Complex **8** was characterized by liberation and identification of **9**.[9a]
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Andrea Sanders, Warren P. Giering*
Department of Chemistry, Boston University
Boston, Massachusetts 02215

Received August 23, 1974

Chemical Reaction Paths. V. The SN1 Reaction of Tetrahedral Molecules

Sir:

In previous papers we have applied what we might call the principle of structural correlation[1] to map minimum energy pathways for a ligand exchange reaction (SN2 at tetrahedral Cd^{II})[2] and for nucleophilic addition to carbonyl groups.[3,4] We now report some new results concerning the chemical reaction path for the SN1 type of reaction.

Tetrahedral molecules that are known or expected to show T_d symmetry as isolated particles usually deviate from this symmetry in a crystal environment. A preliminary survey of the crystal structure data indicated that the more severe distortions are mainly of two types,[5] one maintaining approximate C_{2v} symmetry, the other approximate C_{3v} symmetry. We limit ourselves here to the latter type of deformation since fewer independent parameters are involved, and it is more directly relevant to the SN1 type of reaction.

The parameters describing MX$_4$ and YMX$_3$ groups with C_{3v} symmetry are shown in Figure 1a. The experimental sample points[6] for SO_4^{2-}, PO_4^{3-}, and $AlCl_4^-$ tetrahedra from a wide variety of crystal structures show a common trend (b, c, d); as the axial bond distance r_2 increases, the central atom comes closer to the plane of the other three bonds, which become shorter. Results from YSO$_3$, YPO$_3$, and YSnCl$_3$ species are shown in Figure 1e, f, and g. The correlation of r_1 or r_2 with θ is in all cases very similar to that in the corresponding MX$_4$ species.[7] Indeed, if all sample points (about 200) for the species YAlCl$_3$, YSO$_3$, YPO$_3$, OPX$_3$, YSnCl$_3$, YGeCl$_3$, YSiCl$_3$, YSnBr$_3$, YSnPh$_3$, YPF$_3$, YPCl$_3$, and YPPh$_3$ are referred to a common origin (h) by replacing r_1 by $\Delta r_1 = r(\text{MY}) - r_t(\text{MY}_4)$ and r_2 by $\Delta r_2 = r(\text{MX}) - r_t(\text{MX}_4)$ where r_t refers to the corresponding T_d species,[9] all the Δr_1, θ points lie close to one curve and all the Δr_2, θ points close to another;[10] i.e., all these tetrahedral molecules deform along the same path in the subspace maintaining C_{3v} symmetry!

A simple model, based on three arbitrary assumptions, leads to the observed Δr_1, θ *and* Δr_2, θ relationships: (1) $\Delta r_i = -c \log n_i$, where n_i is Paulings "bond number";[11] (2) $n_2 + 3n_1 = 4$ is assumed to hold for all the tetrahedral molecules in question; (3) the displacement Δ of the central atom from the plane of the three basal ligands is a measure of n; when $\Delta = \Delta_t$ (regular tetrahedron), $n_2 = 1$, when $\Delta = 0$ (trigonal planar molecules) $n_2 = 0$. We find that $n_2 = (\Delta/\Delta_t)^2 = 9 \cos^2 \theta$, $n_1 = 4/3 - 3 \cos^2 \theta$, reproduce the ob-

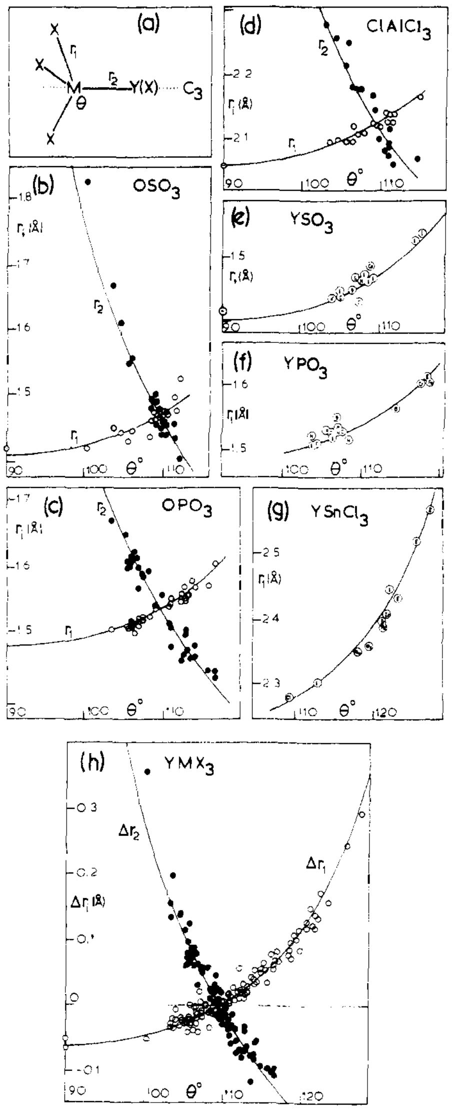

Figure 1. (a) Definition of symbols. (b–g) Sample points for various tetrahedral molecules mentioned in text. (h) All data referred to common origin. The black circles show r_2, ϑ, the open ones r_1, ϑ. Letters in open circles correspond to element Y in YMX_3 species (E = electron pair, ⊖ = planar MX_3). The smooth curves are described in the text.

served trends.[12] Indeed, all the smooth curves shown represent the same pair of functions $\Delta r_2 = -0.5 \log (9 \cos^2 \theta)$, $\Delta r_1 = -0.5 \log (4/3 - 3 \cos^2 \theta)$. Least-squares fitting to four separate subsets of the data yields $c = 0.49$ ($AlCl_4^-$), 0.51 (SO_4^{2-}), 0.47 (PO_4^{3-}), and 0.48 Å ($SnCl_4$), equal within experimental error.

The extrapolation to infinite Δr_2 for $\theta = 90°$ is a property of our model, not of the experimental data, which are just as compatible with a finite intersection at a Δr value of 1 Å or more. More extensive data for very deformed YMX_3 species with $\theta < 100°$ would be needed to fill the gap.

Within the framework of our working hypothesis[1] the close similarity between the plots suggests that important features of the Born-Oppenheimer surfaces of the tetrahedral molecules discussed here are relatively insensitive to the nature of the central atom and of the ligands.[13]

The observed deformations are analogous to those expected for the SN1 type of reaction; that is, they correspond to heterolytic weakening and ultimately fission of the axial bond to give a planar MX_3 species, e.g., the Lewis acids $AlCl_3$ and SO_3 (for which the corresponding sample points are also given). The r_1, θ curves for YMX_3 species may also be interpreted in terms of removing an electron pair from a tricoordinated pyramidal MX_3 unit, e.g., $SO_3^{2-} \rightarrow SO_3 + 2e^-$. The sample points that map this oxidation process lie on the same curve as those mapping the SN1 dissociation of MX_4. Apart from their relevance to the SN1 reaction path, these curves can be used to predict unknown structures of tetrahedral molecules without recourse to any theory of bonding.

Structural data for hydrides are mostly unreliable. Accurate information about deformations of tetrahedral carbon atoms is sparse. However, the relevant parameters from the recent electron-diffraction analysis of *tert*-butyl chloride[15] lie very close to our curves, which encourages us to believe that they are also a fair approximation to the path for the well-known SN1 dissociation of this molecule.

Acknowledgment. One of us (P.M.R.) is indebted to the CIBA-GEIGY (U.K.) Fellowship Trust for the award of a Senior Fellowship.

References and Notes

(1) We have assumed as a working hypothesis that if a correlation can be found between two or more independent parameters describing the structure of a given structural fragment in a variety of environments, then the correlation function maps a minimum energy path in the corresponding parameter space. As Professor L. S. Bartell has pointed out to us, it is difficult to decide whether the correlation function maps a minimum energy path in the parameter space of the isolated structural fragment or a path which describes the response of the given fragment to external forces. The latter kind of path may be even more relevant to the chemical reaction path than the minimum energy path.

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(5) Other authors, e.g., W. S. McDonald and D. W. J. Cruickshank, *Acta Crystallogr.*, 22, 37 (1967); I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A*, **29**, 266 (1973); G. A. Lager and G. V. Gibbs, *Am. Mineral.*, **58**, 756 (1973); W. H. Baur, *Acta Crystallogr., Sect. B*, **30**, 1195 (1974), have also described and analyzed distortions of tetrahedral molecules observed in crystals. Our approach, however, is basically different from theirs.

(6) Full details concerning the choice of examples and the handling of the experimental data taken from the literature will be given elsewhere. However, it may be noted here that even for an arbitrary distortion of a regular tetrahedron, components preserving C_{3v} symmetry can always be separated out by taking appropriate linear combinations of the distance and angle displacement parameters.

(7) The pyramidality of the MX_3 units in YMX_3 clearly depends on the electronegativity of Y. Ligands of high electronegativity, e.g., F, produce flattened MX_3 units, those of low electronegativity, e.g., lone pair, produce pyramidal ones, in agreement with Gillespie's ideas (ref 8). The $YSnCl_3$ sample points, although drawn from a very miscellaneous range (e.g., $SnCl_4$, π-$(C_5H_5)Fe(CO)_2SnCl_3$, $CsSnCl_3$, etc.), still lie close to a well-defined path.

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(9) The r_1 values cover a very wide range, from 1.48 Å (SO_4^{2-}) to 2.41 Å ($SnBr_4$).

(10) The available data for YBF_3, $YAlBr_3$, $YSiF_3$, $YGeBr_3$, $YSnMe_3$, YSF_3, and $YClO_3$ are meager or inaccurate but show the same general trend.

(11) Although assumption 1 lacks any theoretical basis it appears to be a useful crutch for correlating interatomic distances involving a common atom (ref 2, 3, 4).

(12) . . . . and satisfy the conditions imposed by symmetry. Incidentally, the quadratic relationship between r_2 and Δ also leads to much better agreement between observed and calculated C· · ·O distances than the linear dependence assumed in our earlier study of N· · ·C=O interactions (ref 3).

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(16) On leave from the University of Stirling, Scotland.

Peter Murray-Rust,[16] Hans-Beat Bürgi, J. D. Dunitz*
Laboratories of Inorganic and Organic Chemistry
Federal Institute of Technology
Zürich, Switzerland
Received August 30, 1974