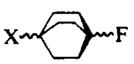
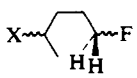
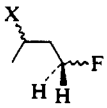
Table I. Substituent Chemical Shifts[a] in Substituted 1-Fluoroalkanes

Compound	SCS[a] in solvent		Δδ (esterification)
	$CFCl_3$	CF_3CO_2H	
$CH_2OH(CH_2)_2F$	3.99	7.54	2.09
$CH_3CHOH(CH_2)_2F$	2.50	6.44	1.72
$CH_3CHOH(CH_2)_3F$	−0.51	2.75	1.63
$CH_3CHOH(CH_2)_5F$	−0.21	1.61	0.50
$CH_3CHOT_s(CH_2)_2F$	2.45	4.78	
$CH_3CHOT_s(CH_2)_3F$	1.29	4.52	
$CH_3CHOT_s(CH_2)_5F$	0.12	3.10	
$CH_2(O_2CCF_3)(CH_2)_2F$		9.63	
$CH_3CH(O_2CCF_3)(CH_2)_2F$		8.16	
$CH_3CH(O_2CCF_3)(CH_2)_3F$		4.38	
$CH_3CH(O_2CCF_3)(CH_2)_5F$		2.11	

[a] Positive values for substituent chemical shifts (SCS) are expressed as parts per million upfield from the average value for 1-fluorohexane and 1-fluorodecane. The chemical shifts of these reference compounds in parts per million upfield from fluorotrichloromethane were found to be respectively: 219.22 (in $CFCl_3$), 212.41 (in CF_3CO_2H), 219.27 (in $CFCl_3$), and 212.59 (in CF_3CO_2H).

Table II. Substituent Chemical Shifts of Acyclic and Bicyclic Fluorides

				
X	SCS[a]	X	SCS[b]	SCS[b]
H	0.00	H	0.00	0.00
$CO_2C_2H_5$	4.47	OH	−0.51	2.50
F	9.23	$OSO_2C_6H_4CH_3$	1.29	2.45

[a] Parts per million in CCl_4. [b] Parts per million in $CFCl_3$.

electrical effects of substituents on ^{19}F shifts in aryl fluorides[4] and more recently in alicyclic and bicyclic fluorides[5,6] is a subject of controversy. A study of aliphatic fluorides potentially may resolve some of the issues involved. In methyl fluorides the expected deshielding effect is observed when the hydrogens of methyl fluoride are successively replaced by electronegative groups. However, in very recent studies of polycyclic and bicyclic molecules the effect of more remote electronegative substituents was a shielding effect in each instance.[5,6]

The chemical shifts of our electronegatively substituted aliphatic monofluorides, calibrated on a Varian A-56/60 spectrometer, are given in Table I. Chemical shifts were obtained for 20, 10, and 5% solutions in fluorotrichloromethane or trifluoroacetic acid (containing 2% fluorotrichloromethane as internal reference) and extrapolated to infinite dilution. The column labeled Δδ (esterification) gives the difference in chemical shift between the alcohols (taken approximately 2 min after mixing with trifluoroacetic acid) and their corresponding trifluoroacetate esters formed by slow reaction with the solvent (taken after several hours). Any solvent effect of water upon chemical shifts should have been approximately nullified by extrapolation to infinite dilution.

The upfield (positive) shift with electron-withdrawing substituents, observed for most of our compounds, and also for the alicyclic and bicyclic fluorides,[5,6] is not easily rationalized on the basis of empirical knowledge or theoretical predictions. That this shift for our compounds is not simply a function of chain length is indicated by a published study[7] in which the chemical shift of the 1-fluoroalkanes from 1-fluoropropane through 1-fluoroheptane was found to vary by less than ±0.4 ppm.

Representative substituent chemical shifts in nonpolar solvents for the bicyclooctanes[6] and for selected examples of our compounds are compared in Table II. Anderson and Stock[5] discussed the possible origin of their upfield shifts, noting that "the positive SCS may be rationalized on the basis of the idea that there is an important repulsive interaction between the more electropositive bridgehead carbon atoms of the bicyclic molecules, leading to an elongation of the structure and an increase in the p character of the endocyclic carbon–carbon bonds." Although such an effect would indeed tend to pull the bicyclic C–C bonds (shown dark in the heading of Table II) nearer to 90°, it is not at all clear that a similar distortion of the C–C and C–H bonds (*cf.* Table II) in our acyclic compounds would occur. On the other hand, the remarkable ability of trifluoroacetic acid to increase the magnitude of substituent chemical shifts (*cf.* Table I) could be explained by changes in conformer populations and the attendant bond anisotropy effects. A possible explanation is that trifluoroacetic acid may hydrogen bond both to the oxygen-containing substituent[8] and to the fluorine,[9] increasing the mutual repulsion of the electronegative groups and increasing the population of elongated conformers.

Our preliminary results clearly point to the need for much more extensive studies of aliphatic fluorine chemical shifts in series of polar and nonpolar, protic and aprotic solvents, which should definitely include trifluoroacetic acid. Additional studies (by P. E. P.) are in progress.

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(10) NASA Trainee, St. Louis University, 1964–1967. The research reported in this paper was supported in part by NASA Traineeship Grant NsG(T)-74 and in part by NSF 7 Grant GP291.

(11) Contribution No. 1533.

Paul E. Peterson, Ronald J. Bopp[10]
Department of Chemistry, St. Louis University
St. Louis, Missouri 63103

William A. Sheppard
Central Research Department,[11] *Experimental Station*
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received December 21, 1968

A Symmetry Rule for Predicting Molecular Structure and Reactivity

Sir:

Symmetry considerations have proved to be a powerful means of predicting the course of certain chemical reactions. The Woodward–Hoffmann rules are outstanding examples.[1] Recently Eaton[2] has proposed similar rules for reactions of transition metal complexes.

In an important paper, which appears to have been largely overlooked, Bader[3] outlined a symmetry rule for predicting the specific way in which any molecule will decompose upon activation. Such a rule is potentially of great value since, in principle, it can be applied to all molecules. The purpose of this note is to call attention to the Bader rule and to show how its usefulness can be extended.

The basis of the rule is the second-order Jahn–Teller effect.[4] The first-order effect[5] deals with degenerate electronic states and actually has not been of great chemical significance. The second-order effect deals with electronic states that are merely close to each other (within about 4 eV) and concerns a very much larger number of molecules. Using second-order perturbation theory, the energy of a molecule, after a small distortion from the stable configuration, can be written as[3]

$$E = E_0 + \frac{1}{2}V_{00}Q^2 + \sum_k \frac{V_{0k}^2}{E_0 - E_k}Q^2 \tag{1}$$

where Q is a normal coordinate for the distortion, E_0 is the undistorted energy, and E_k's are the various excited state energies. Also we have the expressions

$$V_{00} = \int \psi_0(\partial^2 V/\partial Q^2)\psi_0 \, d\tau$$

$$V_{0k} = \int \psi_0(\partial V/\partial Q)\psi_k \, d\tau$$

where ψ_0 is the ground-state wave function, ψ_k is an excited-state wave function, and V is the nuclear–nuclear and nuclear–electronic potential energy.

The first correction, $\frac{1}{2}V_{00}Q^2$, is always positive and the second correction, $\Sigma[V_{0k}^2/(E_0 - E_k)]Q^2$, is always negative. If the latter is comparable in size to the former, reaction along the coordinate corresponding to Q will occur with low (or zero) activation energy. As Bader has shown,[3] only the lowest lying excited state (or two or three states, if very close) seems to be important in the summation of eq 1. The symmetry properties are then brought in by realizing that the integral V_{0k} only has a nonzero value if the direct product of the representations of ψ_0 and ψ_k contains the representation of the displacement Q. Hence the symmetries of the ground electronic state and the lowest excited electronic state(s) determine which kind of nuclear displacement occurs most easily, *i.e.*, the mode of decomposition or rearrangement of the molecule.

The symmetry properties of electronic states can only be expressed at the present time in terms of molecular orbital theory. The representation of $\psi_0\psi_k$ is then the same as that of $\Phi_i\Phi_j$, where Φ_i is the MO occupied in ψ_0, and Φ_j is the MO occupied in its place in ψ_k.[3] They correspond to the highest occupied and lowest unoccupied MO's and are just the levels with which visible and uv spectroscopy is concerned.

Accordingly, any molecule with a big energy gap between those levels is predicted to be quite stable toward chemical change. Equivalently, we can say that colored substances are more reactive than colorless substances. The most interesting applications of Bader's rule should be to substances that are known to have low-lying excited states, or those that are known to interconvert readily from one form to another. An example is provided by $\mathrm{XeF_6}$, where Bartell and Gavin[6] have shown that an excited state of the appropriate symmetry lying 3.5 eV above the ground state leads to a fluctuating structure.

As a further example, consider the possible isomerization of four-coordinated complexes of the transition metal ions between tetrahedral ($\mathrm{T_d}$) and square-planar ($\mathrm{D_{4h}}$) structures. The normal mode which takes a tetrahedral structure into a planar one is of E symmetry.[7] The molecular orbital scheme (needed to express the symmetries) is generally agreed to be

$$(\mathrm{t_1}) \quad \text{or} \quad (\mathrm{t_2})\,\vdots\,(\mathrm{e})(\mathrm{t_2})\,\vdots\,(\mathrm{a_1})$$

with the d manifold separated by dashed lines.[8]

Since $\mathrm{T_1}$ (or $\mathrm{T_2}$) $\times$ E = $\mathrm{T_1 + T_2}$, there is no low-lying transition which causes a tetrahedral complex to rearrange to a planar complex. This is true for all systems from $\mathrm{d^0}$ to $\mathrm{d^{10}}$.

However, first-order Jahn–Teller effects are important for many of these complexes. Only $\mathrm{d^0}$, $\mathrm{d^2}$, high-spin $\mathrm{d^5}$, $\mathrm{d^7}$, and $\mathrm{d^{10}}$ complexes have $\mathrm{A_1}$ or $\mathrm{A_2}$ ground states and are stable. All others are E, $\mathrm{T_1}$, or $\mathrm{T_2}$ states. Since $\mathrm{E \times E = A_1 + A_2 + E}$, and $\mathrm{T_1 \times T_1 = T_2 \times T_2 = A_1 + E + T_1 + T_2}$, all of these allow a distortion in the direction leading toward a planar structure.[9]

Since a $\mathrm{D_{2d}}$, or distorted tetrahedral structure, is sufficient to lift the orbital degeneracy in every case except low-spin $\mathrm{d^3}$, we cannot tell whether the initial distortions will continue on to a planar structure. To get further information we must now look at the stability of the possible planar forms.

The generally agreed on MO scheme for $\mathrm{D_{4h}}$ symmetry is[8d,10]

$$(\mathrm{a_{2g}})(\mathrm{b_{2u}})\,\vdots\,(\mathrm{a_{1g}})(\mathrm{e_g})(\mathrm{b_{2g}})(\mathrm{b_{1g}})\,\vdots\,(\mathrm{a_{2u}})$$

The vibration which takes a planar complex into a tetrahedral one is of $\mathrm{B_{2u}}$ symmetry.[11] The transitions which can give the correct symmetry are $(\mathrm{b_{2u}}) \rightarrow (\mathrm{a_{1g}})$ and $(\mathrm{b_{1g}}) \rightarrow (\mathrm{a_{2u}})$. It seems likely that the energy gap in both cases is only 2–3 eV.[10]

This leads to the conclusion that low-spin $\mathrm{d^2}$, $\mathrm{d^4}$, $\mathrm{d^5}$, $\mathrm{d^6}$, $\mathrm{d^7}$, and $\mathrm{d^8}$ complexes are stable as square-planar structures. Low-spin $\mathrm{d^3}$ is orbitally degenerate. In all other cases an excitation is possible which favors the $\mathrm{B_{2u}}$ vibra-

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Table I. Stable Structures for MX_4 Systems

	High spin	Low spin		High spin	Low spin
d^0	T_d	T_d	d^6	D_{2d}	D_{4h}
d^1	D_{2d}	D_{2d}	d^7	T_d	D_{4h}
d^2	T_d	D_{4h}	d^8	D_{2d}[b]	D_{4h}
d^3	D_{2d}	[a]	d^9	D_{2d}	D_{2d}
d^4	D_{2d}	D_{4h}	d^{10}	T_d	T_d
d^5	T_d	D_{4h}			

[a] Less than D_{2d} symmetry. [b] Spin-orbit forces can remove the first-order Jahn–Teller effect. $NiCl_4^{2-}$ has T_d symmetry: L. Sacconi, *Transition Metal Chem.*, 4, 199 (1968).

tion. This means a low, or zero, activation energy for conversion into either D_{2d} or T_d symmetry. In combination with the conclusions from the first-order Jahn–Teller effects, we can assign a most stable structure for each four-coordinate system according to the number of d electrons and the spin state. Table I summarizes the results for all systems.

The predictions are in accord with experimental facts where known. Note that the conclusions for D_{4h} are based on no interaction with other groups above and below the plane. Such interactions could raise the (a_{2u}) level markedly and stabilize the planar form. Four simple ligands such as halide or cyanide lead to D_{2d} structures in solution for copper(II) complexes,[12] so that axial solvent perturbations are not sufficient in these cases to create planarity.

It is clear that Jahn–Teller effects can be used to predict the stable structures of molecules in general. In practice an MO scheme is required which need be only qualitatively correct. It also follows that an incorrect MO scheme may predict structures wrongly. A test for stability to second-order Jahn–Teller distortions should always be applied to MO calculations.

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Ralph G. Pearson
Chemistry Department, Northwestern University
Evanston, Illinois 60201

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Cyclic Peroxyesters. II.[1] A Novel Ketene Elimination and Decarboxylation Reaction[2]

Sir:

Acyclic peroxides are reduced by phosphines and phosphites into the corresponding deoxy derivatives.[3] The equation below illustrates this general oxygen extrusion reaction for acyclic peresters and triphenylphosphine.[4] However, only few cyclic peroxides have been

$$RCO_3\text{-}t\text{-}Bu + (C_6H_5)_3P \rightarrow RCO_2\text{-}t\text{-}Bu + (C_6H_5)_3PO$$

submitted to this reaction. For example, ozonides are reduced to ketone products,[5] ascaridole is converted to its endooxide,[3a] while phthalic anhydride is formed from phthaloyl peroxide[6] when these cyclic peroxides are treated with triphenylphosphine. In this communication we describe an unusual fragmentation reaction resulting from the reduction of β-peroxylactones by trivalent phosphorus.

The union of equimolar amounts of β-alkyl-β-phenyl-β-peroxypropiolactone (**1**) and triphenylphosphine in *n*-hexane at room temperature leads to quantitative precipitation of triphenylphosphine oxide and the evolution of a gas. Examination of the reaction mixture by vapor phase chromatography indicates the presence of α-alkylstyrene (**2**) and alkyl phenyl ketone (**3**). Infrared analysis shows in addition small quantities of β-alkyl-β-phenyl-β-propiolactone (**4**), as evidenced by its characteristic carbonyl stretching frequency at 1830 cm^{-1}. This thermally labile product does not survive gas chromatographic analysis and decomposes into carbon dioxide and the substituted styrene (**2**).[7] The product composition of this novel fragmentation reaction is illustrated in Scheme I. As indicated in this scheme, the formation of ketone product requires that ketene is present in the gaseous products besides carbon dioxide. Indeed, the ketene was trapped by menthol, benzyl alcohol, and phenol and identified by means of infrared spectra and retention times with the authentic acetates.

In order to elucidate the mechanism of this unprecedented ketene elimination and decarboxylation reaction, the effect of the solvent, the β-alkyl substituent of the peroxylactone, and the nucleophilic character of the triarylphosphine were examined. The quantitative product data are summarized in Table I. In all cases a quantitative balance in terms of styrene (**2**) and ketone (**3**) products was obtained. The product data show that with increasing size of β-alkyl substituent the proportion of ketene elimination is increased over decarboxylation (entries 1–4 in Table I) On the other hand, the proportion of decarboxylation is increased over ketene elimination with increasing polarity of the solvent (entries 4–7 in Table I). Similarly, increasing electron donation by the triarylphosphine substituent (entries 9–11 in Table I) promotes the degree of decarboxylation over ketene elimination.

The kinetics of this reaction was studied by following the rate of disappearance of the characteristic 1810-cm^{-1} carbonyl stretching frequency of the peroxylactone. Most of the triarylphosphines reacted too rapidly with the peroxylactones to provide accurate kinetic data, and for this reason the phosphites were used. Since triphenyl phosphite (entry 8 in Table I) gave the same products as the triarylphosphines, the use of the phosphites to study the kinetics of this reaction is justified.

The kinetic data, summarized in Table II, were obtained by running the reaction directly in a thermally equilibrated infrared cell, using the variable temperature accessory of Barnes Engineering Co. The wavelength drive mechanism of the Perkin-Elmer 237B Infracord was locked at the desired frequency, and the signal output was relayed to a Heath servorecorder using the ordinate scale expansion accessory. The rate constants in Table II were computed from the kinetic runs using an IBM 1130 computer. The reaction follows the second-order rate law, first order in both the peroxide and nucleophile, through

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