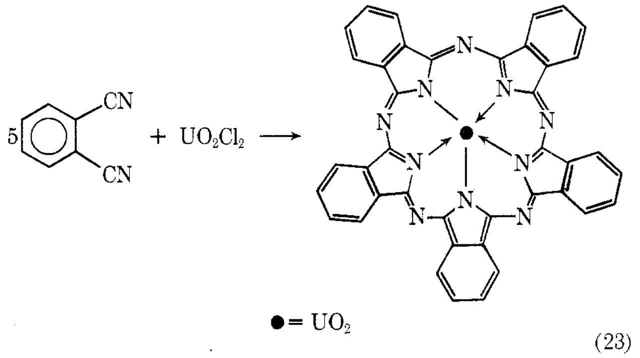
plate leads to an expanded "superphthalocyanin", eq 23.[50] The molecular structure of this remarkable complex is shown in Figure 6.[50a] The strong preference of the uranyl ion to achieve a pentagonal-bipyramidal or hexagonal-bipyramidal coordination geometry has doubtless altered the normal course of the cyclization. The new ligand has a high specificity for the uranyl ion.[51] The scope of this type of transformation is under investigation. Surely a wealth of new compounds, reactions, and useful applications awaits the explorer of actinide organometallic chemistry.



(23)

This work would not have been possible without the generous financial assistance of the National Science Foundation (GP-30623X, GP-43642X), the Research Corporation, the Paint Research Institute, and the Alfred P. Sloan Foundation. It is a pleasure to acknowledge my stalwart co-workers Richard D. Ernst, William J. Kennelly, John R. Kolb, Afif M. Seyam, Djordje R. Stojakovic, William A. Wachter, and Michael R. Walczak, as well as the stimulating structural collaboration of Professors Victor W. Day and Kenneth N. Raymond.

(49) (a) A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, **7**, 27 (1965); (b) F. A. Moser and A. L. Thomas, "Phthalocyanine Compounds", Reinhold, New York N.Y., 1963.

(50) (a) V. W. Day, T. J. Marks, and W. A. Wachter, *J. Am. Chem. Soc.*, **97**, 4519 (1975). (b) The *Chemical Abstracts* name for this complex is 5,35:14,19-diimino-7,12:21,26:28,33-trinitrilopentabenzo[*c,h,m,r,w*][1,6,11,16,21]-pentaazacyclopentacosinatodioxouranium(VI). (c) F. Lux, *Proc. Conf. Rare Earth Res., 10th, 1973,* 871 (1973). (d) J. E. Bloor, J. Schlabitz, C. C. Walden, and A. Demerdache, *Can. J. Chem.*, **42**, 2201 (1964).

(51) (a) T. J. Marks and D. R. Stojakovic, *J. Chem. Soc., Chem. Commun.*, 28 (1975); (b) D. R. Stojakovic and T. J. Marks, manuscript in preparation.

Silver-Assisted Reactions of Chloroformates: A New Route to Reactive Carbocations

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Of the many different ways of effecting substitution, elimination, and rearrangement at carbon, reactions of amines with nitrosating agents generally produce the greatest variety of products and therefore are considered to involve the least discriminating and most reactive intermediates.[1] Although interpretations differ as to how the reaction mechanism should account for the product diversity, there seems to be agreement that reactive carbocations are involved and that the essence of the contrast between deaminations and more conventional substitutions, eliminations, and rearrangements lies in the unusually large driving force for the loss of nitrogen from a diazonium ion or its formal equivalent.[1,2] On that basis, it might be expected that other reactions in which a stable nonnucleophilic leaving group can be formed would also provide reactive carbocations. Analogies have, in fact, been suggested between the loss of nitrogen in deaminations and losses of carbon monoxide,[3] carbon dioxide,[4] nitrous oxide,[5] sulfur dioxide,[4a,6] sulfur trioxide,[7] sulfoxides,[8] or metals[9] from a variety of carbocation precursors.

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$$\begin{tikzcd} & RG^+X^- \arrow[d] \arrow[dr] & \\ RGX \arrow[ur] \arrow[dr] & & \text{products of substitution, elimination, and rearrangement} \\ & R^+GX^- \arrow[ur] & \end{tikzcd}$$

$G = N_2, CO, CO_2, N_2O, SO_2, SO_3, SOR_2$, metal

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(1) For a review summarizing early work, see H. E. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," Interscience, New York, N.Y., 1961, pp 120–127.

(2) Current interpretations consider the crucial steps in deamination to be either: (a) formation of a "hot" or "unencumbered" carbocation: R. Huisgen and C. H. Rüchardt, *Justus Liebigs Ann. Chem.*, **601**, 1 (1956); D. Y. Curtin and M. C. Crew, *J. Am. Chem. Soc.*, **76**, 3719 (1954); J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **76**, 4501 (1954); M. Wilhelm and D. Y. Curtin, *Helv. Chim. Acta*, **40**, 2129 (1957); D. J. Cram and J. E. McCarty, *J. Am. Chem. Soc.*, **79**, 2866 (1957); J. T. Keating and P. S. Skell, "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, p 573; (b) partitioning between ionization and direct reaction of the diazonium ion: A. Streitwieser, *J. Org. Chem.*, **22**, 861 (1957); L. Friedman, "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, p 655; or (c) formation of a separated ion pair: E. H. White and D. J. Woodcock, "The Chemistry of the Amino Group", S. Patai, Ed., Interscience, New York, N.Y., 1968, p 440; C. J. Collins, *Acc. Chem. Res.*, **4**, 315 (1971); R. A. More O'Ferrall, *Adv. Phys. Org. Chem.*, **5**, 331 (1967); J. A. Berson, *Angew. Chem., Int. Ed. Engl.*, 1, 779 (1968).

(3) With breakage of a carbon–oxygen bond: P. S. Skell and I. Starrer, *J. Am. Chem. Soc.*, **81**, 4117 (1959); J. Landgrebe, *Tetrahedron Lett.*, 105 (1965).

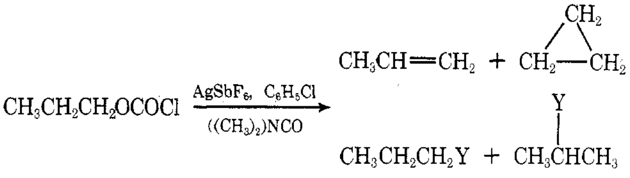
(4) With breakage of a carbon–oxygen bond: (a) P. Beak, R. J. Trancik, and D. Simpson, *J. Am. Chem. Soc.*, **91**, 5073 (1969); (b) D. N. Kevill, W. A. Reis, and J. B. Kevill, *Tetrahedron Lett.*, 957 (1972); (c) W. E. Dupuy, H. R. Hudson, and P. A. Karam, *ibid.*, 3193 (1971); (d) D. N. Kevill, "The Chemistry of Acyl Halides", S. Patai, Ed., Wiley-Interscience, New York, N.Y., 1972, p 381, and references cited therein. With breakage of a carbon–carbon

In this Account, evidence is summarized which establishes that the deamination of amines and the silver(I)-induced reactions of chloroformates proceed via similar product-controlling steps. Moreover, the chloroformate reaction is shown to allow direct comparison with more classically generated species in a way which provides a basis for the proposal that the product diversity from the chloroformate simply reflects branching at the stage of a reactive carbocation. Finally, the reactions of chloroformates with silver(I) are also noted to provide new information about electrophilic aromatic substitution.

Product Comparisons. A correspondence between amine deaminations and chloroformate dehalodecarboxylations was suggested initially because the possible reactive intermediates, the diazonium ion (RN_2^+) and the carboxylium ion[10–13] ($ROCO^+$), would be expected to show similar reactivities. The actual existence of the proposed intermediates is hypothetical in most cases and is, in any event, not critical to a familial resemblance. However, the formation of either or both of these intermediates could involve the slow step of a reaction, so comparisons must be made primarily on the basis of reaction products, although a comparison of qualitative reactivities might also be diagnostic.

Previous studies on *n*-propyl substrates have established that only a few percent rearrangement to isopropyl systems occurs in solvolyses, but that such a rearrangement can account for as much as half the substitution products in deamination and deoxidation. Moreover, in the latter reactions, as much as 10% of the elimination products can be cyclopropane.[2,3]

Reaction of *n*-propyl chloroformate with silver hexafluoroantimonate in chlorobenzene containing 2 equiv of tetramethylurea as a buffer[14] at ambient temperature gives high yields of silver chloride and carbon dioxide, along with isopropylchlorobenzene (5.6%) in an ortho:meta:para ratio of 52:7:41, *n*-propylchlorobenzene (2.4%) in an ortho:meta:para ratio of 47:23:30, cyclopropane (3.9%), propene (47.5%), isopropyl chloride (11.5%), isopropyl fluoride (3.3%), *n*-propyl chloride (13.0%), and *n*-propyl fluoride (3.3%).[4a] Since the reaction of *n*-propyl chloroformate shows that 52% of the substitution products is rearranged and that 8% of the elimination products is cyclized,[15] the dechlorodecarboxylation clearly is similar to deamination and deoxidation in its product-forming stages. Reactions of *n*-propyl chloride and isopropyl chloride with silver hexafluoroantimonate under the same conditions give 1% and 24% silver chloride, suggesting that some of the isopropyl products could arise from subsequent reaction of isopropyl chloride.



$Y = C_6H_4Cl, Cl, F$

The inertness of the bridgehead position in bicyclo[2.2.1]heptanes to most attempts at ionization is classic. The novel substitution of 1-aminoapocamphane upon reaction with nitrosyl chloride served to establish early the idea that the loss of nitrogen provides a large driving force for carbocation formation.[2a,16] The reaction of 1-chloroformylapocamphane with silver hexafluoroantimonate in chlorobenzene at ambient temperature gives 1-chlorophenylapocamphanes in 81% yield and 1-chloroapocamphane in 17% yield. The chloride is inert to further reaction. The ratio of the ortho:meta:para isomers is 39:35:26, and the same mixture of 1-chlorophenylapocamphanes is produced in 9% yield by reaction of 1-aminoapocamphane with nitrosyl chloride and in 19% yield from 1-chlorosulfinylapocamphane and silver tetrafluoroborate.[4a] That these reactions proceed via a 1-apocamphyl cation is established by the fact that the chloroformate reacts with silver hexafluoroantimonate in nitrobenzene to give 1-*m*-nitrophenylapocamphane as the only substituted product, in 24% yield.[17] Moreover, the 1-apocamphyl radical, generated by thermolysis of the diacyl peroxide in chlorobenzene, gives 1-chlorophenylapocamphanes in an ortho:meta:para ratio of 13:60:27, which is substantially different from that obtained from the cation. A similar bridgehead cation may also be generat-

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bond, perhaps prior to formation of the ion: (e) J. J. Keating and P. S. Skell, *J. Am. Chem. Soc.*, **91**, 695 (1969); (f) R. R. Sheldon and J. K. Kochi, *Org. React.*, **19**, 279 (1972).

(5) With breakage of a carbon–nitrogen bond: E. H. White, H. P. Tiwari, and M. J. Todd, *J. Am. Chem. Soc.*, **90**, 4734 (1968); M. P. Doyle and W. Wierenga, *ibid.*, **94**, 3901 (1972); R. H. McGirk and E. H. White, *ibid.*, **95**, 3804 (1973); and references cited therein.

(6) E. S. Lewis and C. E. Boozer, *J. Am. Chem. Soc.*, **74**, 308 (1952); D. J. Cram, *ibid.*, **75**, 332 (1953); C. C. Lee, D. J. Krueger, and D. P. Thornhill, *Can. J. Chem.*, **42**, 1130 (1964).

(7) E. Buncel, *Chem. Rev.*, **70**, 323 (1970).

(8) With breakage of a carbon–oxygen bond of a sulfoxonium species: H. Kwart, E. N. Givens and C. J. Collins, *J. Am. Chem. Soc.*, **91**, 5532 (1969).

(9) With breakage of a carbon–mercury bond: F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **85**, 363 (1963); with breakage of a carbon–copper bond: C. C. Jenkins and J. K. Kochi, *ibid.*, **94**, 843 (1972).

(10) P. Beak, R. J. Trancik, J. B. Mooberry, and P. Y. Johnson, *J. Am. Chem. Soc.*, **88**, 4288 (1966).

(11) This species has been suggested as an intermediate in a variety of reactions of chloroformates and their derivatives. For some cases see: A. Kivinen, *Acta Chem. Scand.*, **19**, 845 (1965); D. N. Clinch and H. R. Hudson, *Chem. Commun.*, 925 (1968); G. A. Olah, Y. Halpern, P. W. Westerman, and J. C. Grant, *J. Org. Chem.*, **39**, 2390 (1974); D. N. Kevill, G. H. Johnson, and W. A. Neubert, *Tetrahedron Lett.*, 3727 (1966); for reactions with silver nitrate: D. N. Kevill and G. H. Johnson, *J. Am. Chem. Soc.*, **87**, 928 (1965); D. N. Kevill and G. H. Johnson, *Chem. Commun.*, 235 (1966); M. J. Zabik and R. D. Schuetz, *J. Org. Chem.*, **32**, 300 (1967); in some cases reaction could be initiated by nucleophilic addition to the carbonyl group without formation of a carboxylium ion.

(12) In Friedel-Crafts reactions aryl chloroformates give the expected aryl ester and alkyl chloroformates give the alkylated products resulting from loss of carbon dioxide: F. A. Drahowzal, "Friedel-Crafts and Related Reactions", G. A. Olah, Ed., Interscience, New York, N.Y.: Vol. II, 1964, p 644; Vol. I, 1963, p 122.

(13) For other suggestions of carboxylium species see: R. J. Crawford and R. Raap, *J. Org. Chem.*, **28**, 2419 (1963); C. Rüchardt and O. Kratz, *Tetrahedron Lett.*, 5915 (1966); T. Koenig, *ibid.*, 2751 (1967); T. Cohen, I. H. Song, J. H. Fager, and G. L. Deets, *J. Am. Chem. Soc.*, **89**, 4968 (1967).

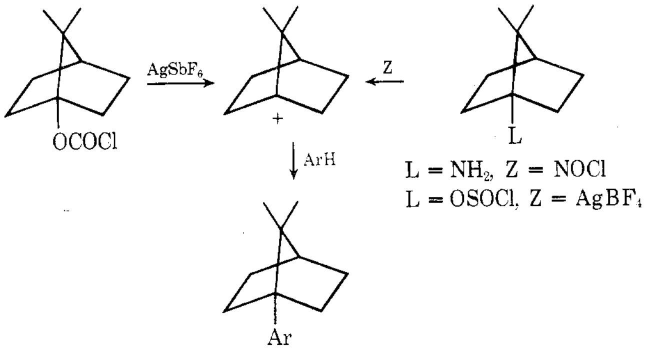
(14) The addition of tetramethylurea to the silver(I) chloroformate reactions in aromatic solvents is generally useful for the generation of reactive cations in a buffered medium. The necessity for tetramethylurea in these reactions was established by the demonstration that, in the absence of such a base, acid initiates alkylation of the aromatic solvent by olefinic products. This difficulty precludes direct comparison of many dechlorodecarboxylations with deaminations even when the latter reaction is alkylation of an aromatic by a sulfinylamine and nitrosyl hexafluoroantimonate.

(15) For a case where a substituted cyclopropane is formed in a thermal decomposition of a chloroformate, see ref 4c.

(16) R. C. Fort, "Carbonium Ions", Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1973, p 1783.

(17) A similar alkylation of nitrobenzene by 1-adamantyl chloroformate has been reported by D. N. Kevill and F. L. Weitl, *J. Am. Chem. Soc.*, **90**, 6416 (1968).

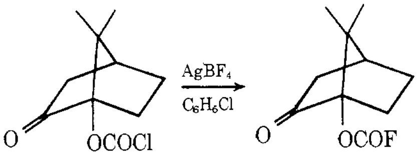
ed from reaction of the unsaturated analog 1-chloroformylapobornylene and silver(I).[18]



L = NH$_2$, Z = NOCl
L = OSOCl, Z = AgBF$_4$

Ar = C$_6$H$_4$Cl; *o* 39, *m* 35, *p* 26
Ar = *m*-C$_6$H$_4$NO$_2$

Attempted generation of analogous bridgehead cations can, however, take other courses. For example, 1-chloroformylapocamphor gives 1-fluoroformylapocamphor in 58% yield upon reaction with silver tetrafluoroborate.[18] Presumably the possible bridgehead cation, which would also be adjacent to a carbonyl group, is of such high energy that the loss of carbon dioxide is precluded.[19]

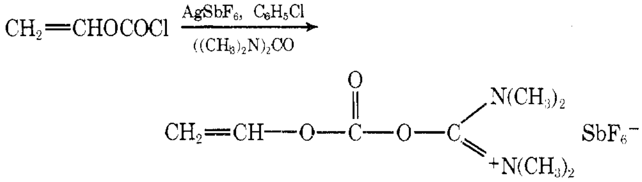


The products from the silver(I)-induced dechlorodecarboxylations of *n*-propyl chloroformate and 1-chloroformyl apocamphane clearly are consistent with the hypothesis that intermediate carbocations generated in those reactions have a reactivity comparable to similar intermediates generated by the reactions of amines with nitrosating agents. The fact that a primary and a bridgehead substrate, structures which are usually inert to ionizations, do react in both cases provides support for the proposition that an appreciable driving force is provided for formation of a carbocation by the simultaneous formation of carbon dioxide.[10,20,21]

Product, reactivity, and formal analogy do not, however, provide a satisfying fundamental explanation of the apparent similarity of dehalodecarboxylations and deaminations. The mechanism of the reaction of the chloroformates needs to be established and the way in which that mechanism differs from processes which have been considered conventional ionizations specified.

Reactive Intermediates. Carboxylium ions and carbocations are logical reactive intermediates for the silver(I)-promoted reactions of chloroformates. A clear-cut mechanistic question is whether carbocation formation occurs concertedly with the formation of carbon dioxide and silver chloride or whether the losses of silver chloride and carbon dioxide are separate processes with a carboxylium ion as an intermediate.[22,23]

The rate studies of Kevill and co-workers suggest the extent of carbon–oxygen and carbon–chlorine bond cleavage in the transition state may vary as a function of the substrate.[4d] Thus benzyl chloroformate reacts with silver perchlorate in benzene at 25 °C 200 times faster than methyl chloroformate, consistent with a positive charge being developed on the carbon of the substrate. Isopropyl chloroformate, on the other hand, undergoes reaction 12 times faster than benzyl chloroformate, although the rates of the corresponding chlorides are reversed by a factor of 60 under the same conditions, suggesting a carboxylium ion contribution. A case in which a novel trapping of an intermediate carboxylium ion appears to occur is the reaction of vinyl chloroformate with silver hexafluoroantimonate in chlorobenzene containing tetramethylurea to give 80% *O*-(carboxyvinyl)tetramethyluronium hexafluoroantimonate.[24]



$$CH_2{=}CHOCOCl \xrightarrow[((CH_3)_2N)_2CO]{AgSbF_6,\ C_6H_5Cl} CH_2{=}CH{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O{-}C\begin{smallmatrix}\nearrow N(CH_3)_2\\ \searrow {}^{+}N(CH_3)_2\end{smallmatrix}\ SbF_6^-$$

Whether or not a carboxylium ion is involved in a reaction of a chloroformate with silver(I) apparently depends on the structure of the chloroformate. If a stable carbonium ion can be directly formed, the carboxylium ion may be by-passed. Even in this mutability the resemblance of the carboxylium ion to the equally elusive diazonium ion is apparent.

If, solely for purpose of discussion, carboxylium

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[18] P. Beak and B. R. Harris, *J. Am. Chem. Soc.*, **96**, 6363 (1974).

[19] In another case the cyclopropyl derivative 1-chloroformyl apotricyclene gives an ortho:meta:para ratio of 1-chlorophenylapotricyclene isomers of 51:26:23, a value which is sufficiently close to the ratio of 50:35:15 produced on pyrolysis of apotricyclene diacylperoxide in chlorobenzene to warrant the suggestion that a bridgehead radical, formed via the cation, is a reaction intermediate.[18]

[20] The rapid reaction of ethyl chloroformate with antimony pentachloride to give mainly ethyl chloride and carbon dioxide releases 21 kcal/mol of heat: G. Olofsson, *Acta Chem. Scand.*, **21**, 114 (1967).

[21] The driving force provided by loss of carbon dioxide is well documented. For some examples, see: (a) in radical formation; T. J. Koenig and T. M. Owens, *J. Am. Chem. Soc.*, **96**, 4052 (1974); W. Adam and G. S. Aponte, *ibid.*, **93**, 4300 (1971); C. Wentrup, *Tetrahedron Lett.*, 2919 (1973); R. W. Hoffman, R. Hirsch, R. Fleming, and M. T. Reetz, *Ber.*, **105**, 3532 (1972); ref 7; (b) in olefin formation: E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963); M. F. Semmelhack and R. D. Stauffer, *Tetrahedron Lett.*, 2667 (1973); M. S. Newman and V. Lee, *J. Org. Chem.*, **38**, 2435 (1973); J. P. White and M. Kim, *Tetrahedron Lett.*, 336 (1974); A. P. Krapcho and E. G. E. Jahngen, *J. Org. Chem.*, **39**, 1650 (1974); D. M. Lemal, E. P. Gosselink, and S. P. McGregor, *ibid.*, **88**, 582 (1966); C. E. Griffin and D. Y. Wysocki, *J. Org. Chem.*, **34**, 751 (1969); (c) in rearrangements: D. S. Tarbell, *Acc. Chem. Res.*, **2**, 296 (1969); H. J. Bestmann and E. Kranz, *Ber.*, **105**, 2098 (1972); (d) in oxidations: D. H. R. Barton, B. J. Garner, and R. H. Wrightman, *J. Chem. Soc.*, 1855 (1966); T. Greilbrokk, *Tetrahedron Lett.*, 1663 (1973); (e) in chemiluminescence: M. M. Rauhut, *Acc. Chem. Res.*, **2**, 80 (1969); N. J. Turro, P. Lechtken, N. E. Schore, G. Schuster, H. C. Steinmetzer, and A. Yekta, *ibid.*, **7**, 97 (1974); E. H. White, E. Rapoport, H. Sliger, and T. A. Hopkins, *Bioorg. Chem.*, **1**, 92 (1971); W. H. Richardson and H. E. O'Neal, *J. Am. Chem. Soc.*, **94**, 8665 (1972); W. Adam and H. Steinmetzer, *Angew. Chem., Int. Ed. Engl.*, **11**, 540 (1972).

[22] Direct observation of the methylcarboxylium ion has been reported: (a) by NMR in SO$_2$ClF: G. A. Olah, P. Schilling, J. M. Bollinger, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 2221 (1974); a sulfur analog is also reported in this paper; (b) by mass spectrometry in the gas phase: P. R. Briggs and T. W. Shannon, *J. Am. Chem. Soc.*, **91**, 4307 (1969).

[23] Carboxylium ions also may be postulated as intermediates in a number of rearrangements and migrations of alkoxycarbonyl groups although alternative pathways are both plausible and usually suggested: R. M. Acheson, *Acc. Chem. Res.*, **4**, 177 (1971); J. A. Berson and R. G. Solomon, *J. Am. Chem. Soc.*, **93**, 4620 (1971); W. Ando, H. Matuyama, S. Nakaido, and T. Migita, *Chem. Commun.*, 1156 (1970); K. Friedrich and H. Straub, *Ber.*, **103**, 3363 (1970); J. Kagan and D. A. Agdeppa, *Helv. Chim. Acta*, **55**, 2255 (1972); P. Schmidt, R. W. Hoffmann, and J. Backes, *Angew. Chem., Int. Ed. Engl.*, **11**, 513 (1972); J. N. Marx, J. C. Argyle, and C. R. Norman, *J. Am. Chem. Soc.*, **96**, 2121 (1974).

[24] P. Beak and J. Barron, *J. Org. Chem.*, **38**, 2771 (1973); in this paper the nucleophilic substitution of vinyl chloroformate by silver trifluoroacetate to give vinyl trifluoroacetate is shown to proceed via the carbonate.

Table I
Products from *trans*-4-*tert*-Butylcyclohexyl Substrates in Acetic Acid

Products	Reactants (%)			
	ROCOCl[a,b]	RCl[a,c]	RN$_2$NHAr[d]	ROSO$_2$Ar[e]
cis-3-*tert*-Butylcyclohexyl acetate	1.3 ± 0.6	3.0 ± 0.3	0.3	1.6
trans-3-*tert*-Butylcyclohexyl acetate	4.6 ± 0.9	3.9 ± 0.6	0.6	0.3
cis-4-*tert*-Butylcyclohexyl acetate	13.0 ± 0.9	14.1 ± 0.9	10.8	21.4
trans-4-*tert*-Butylcyclohexyl acetate	45.6 ± 4.8	2.3 ± 0.6	73.5	0.2
1-*tert*-Butylcyclohexene	9.9 ± 1.5	5.3 ± 1.5		0.4
3-*tert*-Butylcyclohexene	2.1 ± 0.6	6.9 ± 1.8	0.6	4.4
4-*tert*-Butylcyclohexene	23.9 ± 3.6	64.1 ± 15.3	14.1	72.0

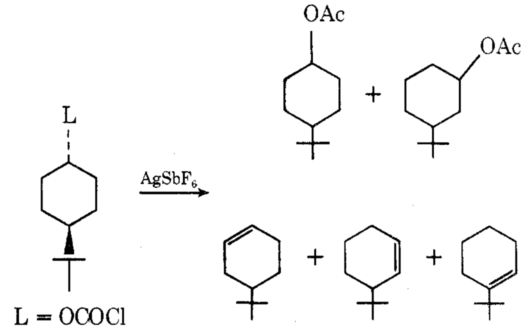
[a] Reaction with silver hexafluoroantimonate at ambient temperature.[27] [b] Yields normalized to 100% excluding chloride products. [c] Yields normalized to 100% from 41% reaction after 48 h.[27] [d] Reaction at 25 °C; yields normalized to 100% from total recovery of ca. 80%; a 0.2% yield of *trans*-4-*tert*-butylcyclohexyl acetate is also reported.[28] [e] Reaction at 25 °C; yields normalized to 100% from a 96% material balance.[29]

and diazonium ions are considered to be the intermediates for the same substrates, the relative leaving group abilities of carbon dioxide and nitrogen might be assessed. In a practical sense it appears that nitrogen is the better; for example, a cation apparently is formed from phenyldiazonium ion,[25] whereas phenyl chloroformate reacts with silver tetrafluoroborate to give phenyl fluoroformate.[4a] However, the conclusions to be drawn from such a comparison should be very limited. Fluoride addition to the chloroformate might precede the loss of silver chloride such that the suggested comparison does not have mechanistic significance. Further work on this question is needed, and it is clear that each case must be investigated in its own right.

The carbocations generated by silver(I)-induced dechlorodecarboxylations of chloroformates and deaminations of amines exhibit high reactivity.[2,4] For example, the 23 and 35% yields of meta-substituted chlorobenzenes noted above from the reactions of *n*-propyl and 1-apocamphyl chloroformates in chlorobenzene are consistent with electrophilic attack by a relatively unselective cation on the solvent.[18,26]

Clearer understanding of the nature of the carbocationic intermediates can come from comparisons of the silver(I)-promoted reactions of other chloroformates and chlorides. If the roles of the substrate, silver(I), and the counterion are similar, such comparisons may reveal how the loss of carbon dioxide affects the course of the reaction. Furthermore, informative comparisons can be made with deaminations and solvolyses.

The products of elimination, substitution, and rearrangement from *trans*-4-*tert*-butylcyclohexyl chloroformate and silver hexafluoroantimonate in acetic acid are presented in the first column of Table I.[27] Deuterium labeling experiments establish that 1-*tert*-butylcyclohexene arises by both consecutive 1,2- and a single 1,3-hydride migration. Oxygen-18 labeling shows that less than 4% of the reaction could involve *trans*-(4-*tert*-butylcyclohexyl)carbonic anhydride. The products from *trans*-4-*tert*-butylcyclohexyl chloride under the same conditions are shown as the second column in the table. The chloride requires 48 h for 41% reaction, while the reaction of the chloroformate is complete in 3 h. Control experiments establish there is essentially kinetic control of the products from the latter reaction, but some further reaction of the initial products could have occurred with the chloride.



Comparison of the product yields in the first two columns of the table clearly shows that the product-determining steps of these reactions are both complex and different in detail. The largest single product from the chloroformate is retained 4-acetate, whereas the chloride gives predominantly olefin, with inverted 4-acetate being the major unrearranged substitution product. The same difference in predominant products is observed on comparison of deamination and solvolysis of the *trans*-4-tert-butylcyclohexyl substrate in acetic acid, as summarized in the third and fourth columns of Table I.[28,29]

The predominant retention from the chloroformate and triazine is consistent with formation of a 4-*tert*-butylcyclohexyl cation, most reasonably, as part of a separated ion pair.[2c,28] The chloride and the sulfonate, on the other hand, appear to react predominately via participation processes, probably involving intimate ion pairs.[30] A complex mechanism could

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(25) C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Am. Chem. Soc.*, **97**, 783 (1975), and references cited therein.

(26) (a) The possibility of equilibration among the isomers was ruled out by control experiments for the reaction of 1-chloroformylapocamphane and by the presence of tetramethylurea for the reaction of *n*-propyl chloroformate; (b) Kevill makes the interesting observation, relevant to the formation of reactive cations from the chloroformates, that in benzene ethyl iodide reacts with silver perchlorate to give only ethyl perchlorate, whereas ethyl chloroformate reacts with silver perchlorate to give 37% ethylbenzene.[4b]

(27) P. Beak, J. T. Adams, and J. A. Barron, *J. Am. Chem. Soc.*, **96**, 2494 (1974).

(28) H. Maskill, R. M. Southam, and M. C. Whiting, *Chem. Commun.*, 496 (1965).

(29) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968).

(30) For analyses of cyclohexyl sulfonates, see J. B. Lambert and G. J. Putz, *J. Am. Chem. Soc.*, **95**, 6313 (1973); J. E. Nordlander and T. J. McCrary, *ibid.*, **94**, 5133 (1972).

Table II
Neighboring Group Participations in the Reactions of *threo*-3-Phenyl-2-butyl Substrates in Acetic Acid

Reactant	Product (total yield, %)	Neighboring group participation (%)[a]			Other processes (%)	Ref
		Phenyl	Methyl	Hydrogen		
ROTs[b]	Acetate, olefin (88)	57		26	17[c]	32
RNH_2	Acetate, alcohol (50)	12	32	24	32[d]	2a, 32
RCl	Acetate, olefin (100)	89		0–11	11[e]	27
ROCOCl	Acetate, chloride (92)	16–21	45	10–19	12–21[f]	27

[a] Normalized to product yields indicated and corrected for recovered reactant. [b] At 75 °C. [c] 7% is attributed to backside displacement by solvent, 10% to ionization. [d] 47% threo alcohol, 50% erythro alcohol. [e] >93% unrearranged olefins which could involve some hydrogen participation. [f] Ca. 50% are erythro products.

be constructed which would rationalize the results of Table I in terms of different extents of ionization and solvent and hydrogen participations for different leaving groups. While such a scheme would be reasonable and internally consistent, the present knowledge of the details of reactions in this system is such that there would be no independent assurance of its validity.

However, reactions of the 3-phenyl-2-butyl substrates are better understood. Indeed, the structure and stereochemistry of the products of rearrangement, substitution, and elimination from the threo and erythro 3-phenyl-2-butyl isomers provide a classic demonstration of the contrasting modes of product control in deamination and solvolyses. In deamination the extent of rearrangement and elimination appears to be attributable to the same factors which control the distribution of conformers in the ground state of the reactant; that situation is commonly termed conformational control.[2] On the basis of analogy to closely related compounds the deamination of 3-phenyl-2-butylamines may be postulated to involve formation of an "open" carbocation prior to the participation steps.[31] Solvolyses of 3-phenyl-2-butyl substrates, on the other hand, appear to proceed largely by initial participation of the neighboring trans phenyl group with participation of the tertiary hydrogen, ionization, and backside displacement by solvent playing lesser roles.[32] The contrast in these reactions may be seen in the different extents of neighboring group participations, which are summarized for the threo isomers from the classic work of Cram et al., in the first two entries in Table II.[2a,32]

The threo isomer of 3-phenyl-2-butyl chloride reacts with silver hexafluoroantimonate in acetic acid at ambient temperature to give only the threo acetate (89%) and (*Z*)-3-phenyl-2-butene (11%), consistent with predominant participation of the trans phenyl group (Table II). Reaction of *threo*-3-phenyl-2-butyl chloroformate with silver hexafluoroantimonate in acetic acid at ambient temperature gives a mixture containing threo acetate (17%), threo chloride (9%), erythro acetate (5%), erythro chloride (1%), 2-methyl-1-phenylpropyl acetate (39%), 2-methyl-1-phenyl-1-propene (4%), and the 3-phenyl-2-butenes (*Z* and *E*, 9% and 4%).[27,33] In order to elucidate the group migrations, the reaction of *threo*-3-phenyl-2-butyl-*1,1,1,3*-d_4 chloroformate was investigated and the location of deuterium in the products was determined. The chlorides are about 35% scrambled, consistent with some trans phenyl participation. The erythro acetates are about 31% scrambled, suggesting cis phenyl migration occurs. These results, including methyl and hydride migrations, are summarized as the fourth entry in Table II. Inspection of the table clearly shows that similar participations occur in dechlorodecarboxylation and deamination and that the product-determining steps in those reactions contrast markedly with those for the chloride or for solvolysis of the tosylate, which are, in turn, similar.

Since *threo*-3-phenyl-2-butyl tosylate has been shown by detailed analysis[32] to lead to products at least 90% by backside participation reactions (k_Δ and k_s), that course may be reasonably assigned to *threo*-3-phenyl-2-butyl chloride. Even in the unlikely case that all the olefin arises from ionization (k_c) of the chloride, the ratio of k_c:($k_\Delta + k_s$) would be 11:89.[34]

The reaction of *threo*-3-phenyl-2-butyl chloroformate provides a more complex picture. The isotopic labeling experiments show that 15–20% of the reaction involves participation by the trans phenyl group ($k_{\Delta Ph}$), 43% methyl migration ($k_{\Delta Me}$), and 9–18% hydrogen migration ($k_{\Delta H}$). At least 3% of the reaction leads to erythro product by a cis phenyl migration, consistent with the intermediacy of a carbocation in which group migration is competitive with bond rotation.[31] The multiplicity of the reaction paths is illustrated by the fact that, while 70% of the threo products involve phenyl participation, 30% arise by some other processes. An obvious intermediate on the latter pathway is also a carbocation. If, for comparison with the chloride, all products which do not involve trans phenyl participation are attributed to initial ionization, the ratio of k_c:($k_\Delta + k_s$) for the chloroformate is 68:20. Although this estimated 28-fold increase in ionization of the chloroformate relative to the chloride is surely not accurate, the significance of the comparison is a clear demonstration that the difference in the reactions of the chloride and chloroformate with silver(I) is attributable to the greater de-

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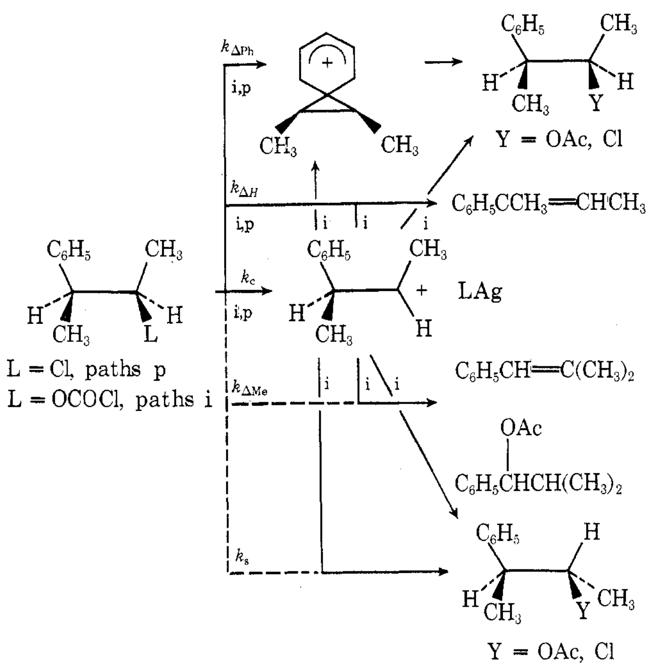
[31] (a) C. J. Collins, *Adv. Phys. Org. Chem.*, **2**, 1 (1964), and references cited therein. (b) The "open" cation is not necessarily free from the influence of its counterion, and is best described as the cationic component of a separated ion pair.[2c]

[32] D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949); C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer, "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, p 1347.

[33] Controls establish that as much as one-third of the initially formed chlorides could react further and that the olefins are not converted to acetates under these conditions. The ketone, 3-methyl-2-phenyl-1-penten-4-one, is also formed in 6% yield as a secondary product.

[34] For a recent discussion of k_Δ, k_s, and k_c analyses, see D. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972); participation does not exclude ion pairs, but does imply crossover does not occur after participation begins.

Scheme I



gree of ionization of the latter.

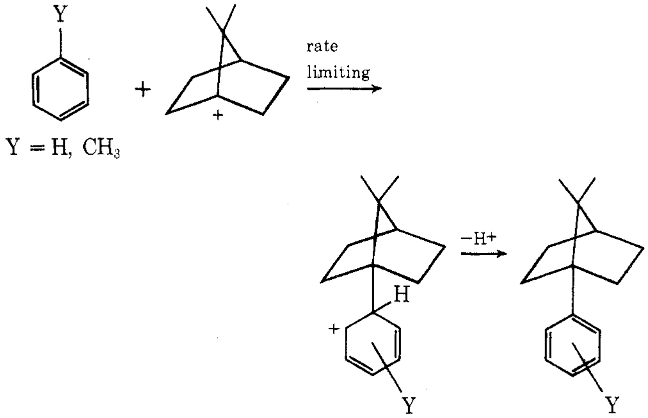
The reaction paths which can be inferred from the product and labeling studies for the reactions of the *threo*-3-phenyl-2-butyl chloride and chloroformate are designated p and i, respectively in Scheme I. The reaction $k_{\Delta \mathrm{Ph}}$ is predominant for the chloride, while the process k_c is dominant for the chloroformate. The dual routes from the chloroformate to the threo and erythro products required by the labeling data are shown by two paths from the carbocation. That intermediate which is the cation component of a separated ion pair should be taken to represent three nonequilibrating rotationally isomeric carbocations formed directly from the conformational isomers of a chloroformate–silver(I) complex precursor. The pronounced methyl migration as well as nonparticipative formation of threo and erythro products and cis phenyl participation to give erythro products can be readily rationalized via such carbocations.[2c,27,31]

Mechanistic Distinctions. The fundamental reason for the resemblance of silver(I)-promoted dechlorodecarboxylations and deaminations is, as expected, the increased driving force for ionization attributable to the losses of stable nonnucleophilic leaving groups in each case. The contrast between those reactions and silver(I)-promoted loss of chloride or solvolyses may be readily understood in terms of predominant reaction of the latter by participation processes. Dechlorodecarboxylations, deaminations, and related reactions[3-9] should not be considered abnormal, but merely reactions in which ionization to give a reactive carbocation can be the major reaction pathway. While such a conclusion is both implicit and explicit in much of the previous work on solvolyses and deaminations,[2,31,32,34,35] these comparisons of chlorides and chloroformates provide cases which are free from the differences in reaction conditions and leaving groups which plague most earlier studies.

The complex product mixtures obtained from the chloroformates relative to the chlorides may be considered a direct consequence of the fact that the carbocations provide a point at which branching readily occurs to a variety of products or intermediates, including those involved in the separate and distinct participations.[34] The fact that the carbocation may reflect the structure of its antecedent states provides a reasonable rationalization for conformational control.[2,31,32,35] This rationalization does not give adequate consideration to the structure of the ion pairs involved or the apparent differences in detail in nominally similar reactions.[2c] Clearly both areas, as well as more quantitative determinations of differences in participations and ionizations, are rich in possibilities for further investigation. However, there appears to be no need at present to explain the differences in products between the chlorides and the chloroformates or between solvolysis and deamination in terms of "hot" or "unencumbered" ions which are not in equilibrium with their environment or by direct partitioning of reactive species prior to the formation of carbocations.

The reaction of chloroformates with silver(I) should prove useful in cases where reactive carbocations are desired or mechanistic information about such species is sought. In particular, this reaction may often be more convenient than the corresponding deamination, and in cases where olefinic products are not stable to deaminative reactions, chloroformate precursors should be preferred.

Applications to Mechanisms of Electrophilic Aromatic Substitutions. Dechlorodecarboxylation has been useful in providing new information about electrophilic aromatic substitutions. The 1-apocamphyl cation, a species which is so reactive[36] that it undergoes electrophilic aromatic substitution on nitrobenzene and attacks benzene faster than toluene, reacts via rate-limiting formation of a σ complex.[18] That result suggests substantial limitations should be placed on extrapolations of the alternative mechanism of rate-limiting π-complex formation suggested to be important with reactive electrophiles.[37]



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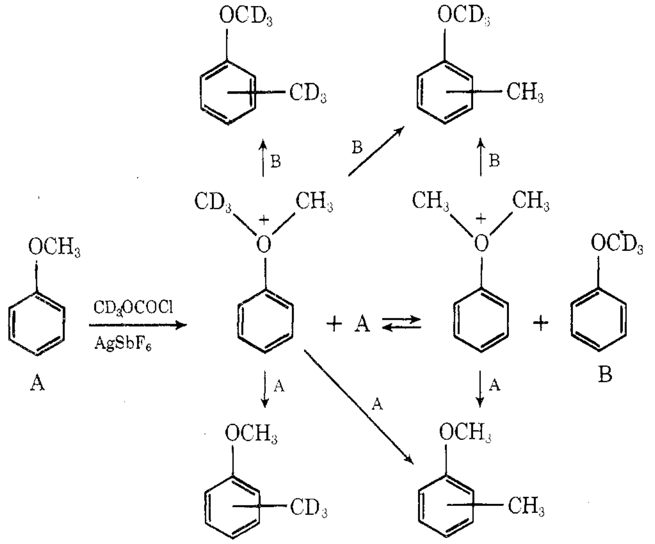
(35) For recent cases: (a) E. White and K. Field, *J. Am. Chem. Soc.*, **97**, 2148 (1975); (b) J. A. Berson, R. T. Luibrand, N. G. Kundu, and D. G. Morris, *ibid.*, **93**, 3075 (1971); (c) C. J. Collins and B. M. Benjamin, *J. Org. Chem.*, **37**, 4358 (1972); (d) W. Huckel and H. J. Kern, *Justus Liebigs Ann. Chem.*, **728**, 49 (1969); (e) D. E. Applequist, M. R. Johnston, and F. Fisher, *J. Am. Chem. Soc.*, **92**, 4614 (1970); (f) H. Hart and J. L. Brewbaker, *ibid.*, **91**, 716 (1969); (g) A. T. Jurewicz and L. Friedman, *ibid.*, **90**, 4466 (1968); (h) T. Cohen, A. R. Naniewski, G. M. Deeb, and C. K. Shaw, *ibid.*, **94**, 1786 (1972); (i) S. J. Cristol, J. R. Mohrig, and G. T. Tiedaman, *J. Org. Chem.*, **37**, 3239 (1972).

(36) For other evidence on the high reactivity of this type of bridgehead ion, see: E. H. White, R. H. McGirk, C. R. Aufdermarsh, H. P. Tiwari, and M. J. Todd, *J. Am. Chem. Soc.*, **95**, 8107 (1973).



The reaction of methyl-d_3 chlorofromate with anisole is interesting because it reveals that the reaction proceeds predominantly by initial attack on the oxygen. The isotopic composition has been determined as a function of time and shown to fit the scheme shown.[38] Moreover, the intermediate methyl(methyl-d_3)phenyloxonium ion does not undergo intramolecular rearrangement to *o*-methylanisole. Since previous recognition of such complexes in electrophilic aromatic substitution has depended on unusual yields of ortho products, these results suggest that the intermediacy of n complexes could be much more general than previously recognized.

The work in my laboratories was carried out by the exceptionally able collaborators named in the footnotes. I am grateful to them, and we are grateful to the National Science Foundation and the National Institutes of Health for support.

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(37) G. A. Olah, *Acc. Chem. Res.*, **4**, 240 (1971); see also: P. Rys, P. Skrabal, and H. E. Zollinger, *Angew. Chem., Int. Ed. Engl.*, **11**, 874 (1972).

(38) P. Beak, J. T. Adams, P. D. Klein, P. A. Szczepanik, D. A. Simpson, and S. G. Smith, *J. Am. Chem. Soc.*, **95**, 6027 (1973).

Geometric Representation of Equilibrium Thermodynamics

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While thermodynamics continues to play a central role in chemistry and other sciences concerned with the thermal properties of matter, the basic formalism for equilibrium thermodynamics largely retains the form which it was given in the latter half of the 19th century, culminating in the work of Gibbs.[1] A recent writer reflects a widespread view in remarking, "We may be reasonably certain that a treatise on, say, thermodynamics, published in the year 2000 will not be fundamentally different from one available today . . .".[2]

New research[3] suggests that this prognosis may be unduly pessimistic. Examination of the formalism of equilibrium thermodynamics has revealed an unexpected facet of the theory, a *geometrical* character which provides a new set of tools for the solution of practical thermodynamic problems. This geometric character is quite distinct from that known to thermodynamicists since the time of Gibbs, but is instead more reminiscent of that of modern gravitation theory, or of quantum theory in Hilbert space.

Because these new developments are of an abstract and mathematical character, it may clarify their significance to refer initially to a quite different area of science—that of quantum mechanics. In quantum theory, certain formal features (by now widely familiar) may be identified which are found to have counterparts in the context of a general theory of thermodynamic equilibrium. The nature of the new thermodynamic work can therefore be suggested by reference to the analogous features of the quantum theory,[4] in particular to the central role of the abstract "scalar products" between abstract "vectors," and the implied geometrical structure. The empirical basis of the Gibbsian formalism will be summarized in a form which reveals how the thermodynamic laws imply, and are implied by, an underlying geometric structure of the theory. Some general features of the resulting geometric formalism of equilibrium thermodynamics will be noted in conclusion.

Quantum Theory and Thermodynamics

Modern quantum theory is known to depend in a fundamental sense on the mathematical properties of Hilbert space, whose intrinsic role in a proper formulation of the theory was stressed particularly by von Neumann.[5] In Schrödinger's wave mechanics, each state

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(1) J. W. Gibbs, "Collected Works", Vol. I, Longmans, Green, and Co., New York, N.Y., 1928.

(2) *Phys. Today*, **27**, 57 1974).

(3) (a) F. Weinhold, *J. Chem. Phys.*, **63**, 2479 (1975); (b) *ibid.*, **63**, 2484 (1975); (c) *ibid.*, **63**, 2488 (1975); (d) *ibid.*, **63**, 2496 (1975); (e) *ibid.*, to be published.

(4) Such similarities allow one, for example, to draw an analogy between the stability conditions of thermodynamics (such as Le Châtelier's principle) and variational inequalities of quantum theory; see, e.g., F. Weinhold, *Adv. Quantum Chem.*, **6**, 299 (1972).