

in ONMnTPP(MPip) is not necessarily a result of a structural trans effect of the NO ligand but rather a stretch resulting from steric interaction.

The most significant difference in the two structures is the manner in which NO coordinates to the metal. Nitric oxide coordinates to manganese in a linear fashion with a MnN₂O angle of 176.2 (5)°; the FeN₂O system is bent with the angle equal to 142.1 (6)°. The manganese complex is isoelectronic with the corresponding carbonyl heme derivative which is expected to have a linear FeCO bond system;¹³ the iron nitrosyl complex has one additional electron. These results are most readily understood in terms of a general bonding model for metal nitrosyl complexes discussed by Mingos.¹⁴ In addition, a molecular orbital model which is compatible with all data on CO, NO, and O₂ complexes of cobalt(II) and iron(II) porphyrins leads to similar predictions.¹⁵

In this bonding scheme, a linear geometry is expected to be more stable for d¹-d⁶ complexes and a bent geometry with a bond angle of ~120° for d⁸ complexes. A bending of the MNO grouping is associated with an energetically more stable bonding ($\pi^*(\text{NO})$, d_{z²}) and a less bonding (d_{z²}, $\pi^*(\text{NO})$) pair of orbitals of σ symmetry; concomitant with the distortion is a destabilization of the (d_{z²}, $\pi^*(\text{NO})$) π -type molecular orbital. The stabilization of ($\pi^*(\text{NO})$, d_{z²}) and the destabilization of (d_{z²}, $\pi^*(\text{NO})$) are both proportional to the MNO angle or distortion. In this d⁷ iron complex, the FeNO angle of ~140° is consistent with a smaller stabilization of the half-filled ($\pi^*(\text{NO})$, d_{z²}) molecular orbital and a correspondingly smaller destabilization of the filled (d_{z²}, $\pi^*(\text{NO})$) molecular orbital compared to the d⁸ complexes.¹⁶ As noted above, the M-N_{NO} bond lengths are consistent with a decreased π interaction in the order Mn > Fe > Co. The structural trans effect is also consistent with this bonding model. Further work on the apparent interrelationship of the MNO angle and the M-N_{NO} π -type interaction is underway.

Acknowledgment. This work was supported by National Institutes of Health, Grant HL-15627, and the Research Corporation.

Supplementary Material Available. A listing of structure factor amplitudes for ONMTPP(MPip) and ONFeTPP(NMeIm) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-5293.

(12) See ref 4 and W. R. Scheidt, J. A. Cunningham, and J. L. Hoard, *J. Amer. Chem. Soc.*, **95**, 8289 (1973), for quantitative discussion of the difficult steric interactions. No such steric interactions (at these distances) are required when 1-methylimidazole is the axial ligand.

(13) V. L. Goedken, J. Molin-Case, and Y.-A. Whang, *J. Chem. Soc., Chem. Commun.*, 337 (1973).

(14) D. M. P. Mingos, *Inorg. Chem.*, **12**, 1209 (1973).

(15) B. B. Wayland, J. V. Minkiewicz, and M. E. Abd-Elmageed, *J. Amer. Chem. Soc.*, **96**, 2795 (1974).

(16) This is also consistent with the structure¹⁷ of the five-coordinate complex ONFeTPP wherein the FeNO bond angle is ~150°.

(17) W. R. Scheidt and M. E. Frisse, to be submitted for publication.

Paul L. Piciulo, Gregory Rupprecht, W. Robert Scheidt*

Department of Chemistry, University of Notre Dame
Notre Dame, Indiana 46556

Received March 14, 1974

Effect of the Cyclopropyl Substituent on the Rates of Electrophilic Additions to Alkenes

Sir:

The interaction of the cyclopropyl group with an adjacent electron-deficient center continues to be a topic of extreme interest.^{1,2} Conspicuously absent among these studies has been a systematic examination of the effect of a cyclopropyl group on the rates of electrophilic addition to alkenes.³⁻⁶

We report herein an investigation of the influence of cyclopropyl on the rates of representative electrophilic additions to ethylenes. The results show accelerations by large factors (*ca.* 1000) for cyclopropyl relative to phenyl when the transition state for addition leads to a relatively open positive charge on the adjacent carbon susceptible to resonance stabilization by the substituent. We find minimal rate differences (factors between one and four) when the substrate contains another strongly stabilizing substituent which preempts the effect of the cyclopropyl or when there is formation of a bridged intermediate which precludes resonance stabilization. Thus the magnitude of the acceleration provides a useful criterion of the transition state structure.

The reaction of vinylcyclopropane with bromine in acetic acid, aqueous sulfuric acid, and *p*-chlorobenzene-sulfonyl chloride in acetic acid and of diethyl α -cyclopropylvinyl phosphate with aqueous HCl were found to proceed as shown in eq 1-4.

The rates are presented in Table I, along with data for the reactions of the corresponding phenyl and *n*-alkyl substituted derivatives for comparison.^{7,9,10} The

(1) (a) D. F. Eaton and T. G. Traylor, *J. Amer. Chem. Soc.*, **96**, 1226 (1974); (b) R. S. Brown and T. G. Traylor, *ibid.*, **95**, 8025 (1973); (c) C. F. Wilcox, L. M. Loew, and R. Hoffmann, *ibid.*, **95**, 8192 (1973); (d) W. J. Hehre and P. C. Hiberty, *ibid.*, **96**, 302 (1974); (e) G. A. Olah and P. W. Westerman, *ibid.*, **95**, 7530 (1973); (f) G. A. Olah and G. Liang, *ibid.*, **95**, 3792 (1973); (g) E. N. Peters and H. C. Brown, *ibid.*, **95**, 2397, 2400 (1973).

(2) (a) G. A. Olah, C. L. Jewell, D. P. Kelly, and R. D. Porter, *J. Amer. Chem. Soc.*, **93**, 146 (1971); (b) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, **87**, 4533 (1965); (c) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973); (d) H. G. Richey in "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley Interscience, New York, N. Y., 1972, p 1295; (e) K. B. Wiberg and A. J. Ashe, *ibid.*, p 1201; (f) M. Charton in "Chemistry of Alkenes," J. Zabicky, Ed., Wiley Interscience, New York, N. Y., 1970, p 511.

(3) For reviews on electrophilic additions to alkenes see (a) R. Bolton in "Comprehensive Chemical Kinetics," Vol. 9, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, London, 1973, p 1; (b) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, London, 1966; (c) R. C. Fahey, *Top. Stereochem.*, **3**, 237 (1968).

(4) There are several cases where the products of electrophilic addition to various cyclopropylalkenes have been studied, but there has been no systematic study of the kinetics of these reactions: (a) R. T. Gray and H. E. Smith, *Tetrahedron*, **25**, 3161 (1969); (b) P. K. Freeman, F. A. Raymond, and M. F. Grostic, *J. Org. Chem.*, **32**, 24 (1967); (c) J. B. Hendrickson and R. K. Boeckman, Jr., *J. Amer. Chem. Soc.*, **93**, 4491 (1971).

(5) The cleavage of cyclopropanes by electrophiles has been extensively examined: (a) R. J. Ouellette, R. D. Robins, and A. South, Jr., *J. Amer. Chem. Soc.*, **90**, 1619 (1968); (b) C. H. DePuy and R. H. McGirk, *ibid.*, **95**, 2366 (1973); **96**, 1121 (1974); (c) C. H. DePuy, A. H. Andrist, and P. C. Fünfschilling, *ibid.*, **96**, 948 (1974); (d) R. T. LaLonde and A. D. Debboli, Jr., *J. Org. Chem.*, **38**, 4228 (1973); (e) P. E. Peterson and G. Thompson, *ibid.*, **33**, 968 (1968).

(6) For the rate of electrophilic hydration of *p*-cyclopropylstyrene see L. B. Jones and S. S. Eng, *Tetrahedron Lett.*, 1431 (1968).

(7) The presence of ring-opened product from the bromination of cyclopropylethylene as determined by Slobodin and coworkers⁸ could result from competitive electrophilic attack on the ring and double bond so that the rate of electrophilic attack on the double bond would be only 60% of the rate of disappearance of olefin. This rate would still be within the limits specified in Table I.

(8) Ya. M. Slobodin and I. Z. Egenburg, *Zh. Org. Khim.*, **5**, 1315

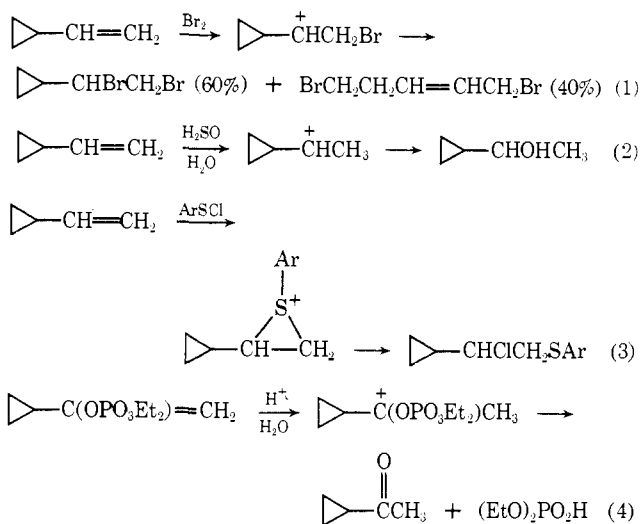


Table I. Rates of Electrophilic Additions to Substituted Alkenes

Alkene	R	Reaction	k_{obsd}	k_{rel}
RCH=CH ₂	c-C ₃ H ₅	Br ₂ , HOAc, 25 ^o ^a	≥ 1.5	>1000
			× 10 ^{4b}	
	Ph		11.2	1.0
	n-Bu		31.7	3
	c-C ₃ H ₅	30.4% H ₂ SO ₄ , 25 ^o ^a	1.866	996
			× 10 ^{-2c}	
	Ph		1.874	1.0
			× 10 ⁻⁵	
n-Bu		61.5 ^b	0.1 ^d	
c-C ₃ H ₅	p-ClPhSCl, HOAc, 25 ^o ^a		3.8	
RC(OPO ₃ -Et ₂)=CH ₂	Ph	0.1 N HCl, 54.7 ^o	16.0	1.0
			33.2	2.1
	n-Bu		4.57	1.4
	c-C ₃ H ₅		× 10 ^{-5 c,e}	
			3.17	1.0
Me			× 10 ⁻⁵	0.4 ^f

^a Measured as in ref 9a. ^b M⁻¹ sec⁻¹. ^c Sec⁻¹. ^d Reactivity relative to phenyl in 48.7% H₂SO₄, ref 9a. ^e Reference 9c. ^f Reactivity relative to the phenyl derivative for hydrolysis of the dimethyl esters in 2 M HClO₄, ref 9e.

bromination of cyclopropylethylene was extremely fast and could barely be observed by the stopped-flow technique used. The reported rate constant is the lower limit.

The rapid rates of bromination and hydration of

(1969); *Chem. Abstr.*, **71**, 90898 (1969); Ya. M. Slobodin and I. N. Shokhor, *Zh. Obshch. Khim.*, **22**, 195 (1952); *Chem. Abstr.* **46**, 10112c (1953).

(9) (a) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. McDonald, *J. Amer. Chem. Soc.*, **95**, 160 (1973); (b) G. H. Schmid, V. M. Cszmadia, V. J. Nowlan, and D. G. Garratt, *Can. J. Chem.*, **50**, 2457 (1972); (c) J. P. Berry, E. P. Lyznicki, K. Oyama, and T. T. Tidwell, to be submitted for publication; (d) R. D. Frampton, T. T. Tidwell, and V. A. Young, *J. Amer. Chem. Soc.*, **94**, 1271 (1972); (e) C. Triantaphylides, G. Peiffer, and R. Gerster, *Bull. Soc. Chim. Fr.* 1756 (1973).

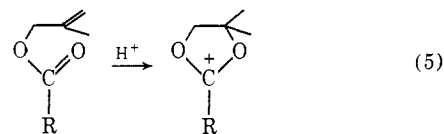
(10) The products of the bromination were reported by Slobodin.⁸ Cyclopropylmethylcarbinol was the only observed volatile product from the hydration reaction but was obtained in only 25% yield, apparently due to polymerization at the higher alkene concentration used for the product study. The sulfonyl halide noted was the only product observed by nmr immediately after mixing the reagents and was identified by its nmr spectrum in CDCl₃ solutions (δ ppm from internal TMS): ¹H (Varian T-60) 0.55 (4, m, C₂H₅), 1.08 (1, m, CH of c-Pr), 3.35 (3, m, CHClCH₂S), 7.27 (4, s, Ar); ¹³C (Varian CFT-20) 4.77 (t, CH₂), 7.20 (t, CH₂), 18.34 (d, CH of c-Pr), 43.15 (t, CH₂S), 66.29 (d, CHCl), 129.12 (d, aryl CH), 131.15 (d, aryl CH), 134.35 (s, aryl CS), and 134.84 (s, aryl CCl).

cyclopropylethylene relative to styrene and 1-hexene indicate that relatively open ions are formed in these reactions so that the intense conjugative ability of the cyclopropyl group can stabilize the adjacent charge. Open ion intermediates are implicated in the accepted mechanisms of these reactions, except for bromination of 1-hexene.^{9a}

Sulfonyl halide addition gives minimal discrimination between the groups, and all the reactions proceed at comparable rates. This is consistent with the fact that sulfonyl halide additions involve cyclic intermediates^{9b} and thus allow very little conjugative stabilization.

The phosphate hydrolyses involve rate-determining protonation of the double bond, followed by hydration and C-O bond cleavage of the phosphate to yield a methyl ketone.^{9c,e} The absence of any cyclopropyl stabilization relative to phenyl or methyl substituents in this reaction shows that the strong stabilizing effect of the adjacent phosphoryloxy group almost completely levels the advantage cyclopropyl has over these groups when cross-conjugated substituents are absent. In solvolysis reactions leveling of rate accelerations due to cyclopropyl and double bonds of 10¹¹ have been observed.¹¹

These results also provide a satisfactory interpretation of the reported formation of 2-substituted dioxolenium ions by protonation of alkenes (eq 5), in which the rela-



tive heats of reaction were the same for methyl and cyclopropyl substituents.¹² The observation¹² that "cyclopropyl stabilizes both the ester and the cation to the same extent" may be ascribed to leveling of the usually strong cation stabilizing effect of cyclopropyl by the cross-conjugated oxygens.

The effect of cyclopropyl on the rates of the additions to olefins is qualitatively correlated with the ρ values for the additions to the corresponding substituted styrenes. Thus bromination and hydration, which show large effects due to cyclopropyl, have ρ values of -4.7¹³ and -3.6,¹⁴ respectively, whereas addition of arylsulfonyl chloride and phosphate hydrolysis show smaller effects of cyclopropyl and have ρ values of lesser magnitude, -2.4¹⁵ and -2.1,^{9d} respectively.

By way of comparison, cyclopropyl groups are generally more potent stabilizing groups than phenyl in solvolysis reactions. For example, cyclopropyldimethylcarbinyl p-nitrobenzoate is 519 times more reactive than cumyl p-nitrobenzoate at 25^o in 80% acetone.¹⁶ This stabilizing effect of cyclopropyl decreases and finally becomes destabilizing when the cyclopropyl group is gradually constrained from the conjugatively favorable bisected orientation relative to the incipient carbonium ion and forced into a perpendicular con-

(11) P. G. Gassman and A. F. Fentiman, Jr., *J. Amer. Chem. Soc.*, **91**, 1545 (1969); **92**, 2549-2551 (1970).

(12) J. W. Larsen and S. Ewing, *J. Amer. Chem. Soc.*, **93**, 5107 (1971).

(13) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 2944 (1970).

(14) W. M. Schubert and J. R. Keeffe, *J. Amer. Chem. Soc.*, **94**, 559 (1972).

(15) W. L. Orr and N. Kharasch, *J. Amer. Chem. Soc.*, **78**, 1201 (1956).

formation.¹⁶ This is consistent with the fact that the cyclopropyl group is acid weakening in benzoic acids, where resonance is possible, but acid strengthening in acetic acids where resonance is unimportant.¹⁷

Thus cyclopropyl gives a widely varying effect on electrophilic additions to olefins. The variation of this effect helps to define the transition state structure for different additions and promises to prove useful as a guide to the evaluation of the mode of attack of different electrophiles on olefins.¹⁸

(16) (a) Y. E. Rhodes and V. G. DiFate, *J. Amer. Chem. Soc.*, **94**, 7582 (1972); (b) B. R. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970); (c) V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

(17) (a) R. C. Hahn, T. F. Corbin, and H. Schechter, *J. Amer. Chem. Soc.*, **90**, 3404 (1968); (b) Y. E. Rhodes and L. Vargas, *J. Org. Chem.*, **38**, 4077 (1973).

(18) After submission of this manuscript a study appeared of the hydrochlorination and oxymercuration of 2-cyclopropyl-3-phenyl-2-

Acknowledgment. Financial support by the National Research Council of Canada is gratefully acknowledged.

butene (G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Amer. Chem. Soc.*, **96**, 3548 (1974)), in which the only observed products appeared to result from preferential generation of the cationic center next to the cyclopropyl group. Also we have learned (A. J. Kresge and C. I. Young, unpublished results privately communicated) that in hydrolysis of vinyl ethers, $RC(OMe)=CH_2$, the rates of hydration are essentially the same when R is cyclopropyl or methyl, and about six times less when R is phenyl. Similarly cyclopropyl has been found to be less effective at assisting the formation of the bridged 2-adamantyl cation than is ethyl (D. Lenoir, *Chem. Ber.*, **106**, 2366 (1973)). All of these results are in complete accord with the interpretations proposed herein.

Dennis G. Garratt, Agnieszka Modro, Kiyotaka Oyama
George H. Schmid, Thomas T. Tidwell,* Keith Yates

Department of Chemistry and Scarborough College
University of Toronto, Toronto, Ontario M5S 1A1, Canada

Received May 8, 1974

Book Reviews

Gas-Chromatographic Analysis of Trace Impurities. By V. G. BEREZKIN and V. S. TATARINSKII (A. V. Topchiev Institute for Petrochemical Synthesis, Academy of Sciences of the USSR, Moscow). Translated from Russian by J. E. S. BRADLEY (University of London, London, England). Consultants Bureau, A Division of Plenum Publishing Corp., New York, N. Y. 1973. ix + 177 pp. \$29.50.

This book discusses the major aspects of gas chromatographic determinations of trace impurities. Methods are discussed in terms of general principles, and specific methods are given only when needed to illustrate the methodology. There is no attempt to give a comprehensive listing of methods for specific materials. The book is intended for those who are unfamiliar with the field of gas chromatographic trace analysis. The authors' treatment of subject matter does, however, assume that the reader has some familiarity with the basic concepts and practices of gas chromatography.

The book opens with a general discussion of the problems associated with gas chromatographic separation of impurities. This is followed by a chapter on the use of large samples to achieve high sensitivity with emphasis on the relationship between sample size and column performance. The next chapter presents a general discussion of gas chromatography detectors with emphasis on ionization and thermal conductivity detectors. A subsequent chapter is devoted to the use of selective sorbents and selective detectors, such as electron capture and flame-photometric detectors. The next topic presented is the use of column temperature programming to enhance trace component separations. This is followed by a chapter on reactive analytical gas chromatography. The next topic discussed is that of sample accumulation or concentration methods. This chapter is subdivided into (1) chromatographic methods of impurity enrichment and (2) other techniques. The latter includes a variety of enrichment methods which are based on adsorption or condensation of trace impurities and can be used in conjunction with analysis by gas chromatography. The factors that must be considered in quantizing gas chromatographic analyses are discussed in the next chapter. The final chapter is devoted to a discussion of basic methods of preparing standard mixtures for calibrating chromatographic systems. Although each chapter is well documented with references, use of the book is hampered by the lack of a subject index.

The book makes one aware of the major problems encountered in performing trace analysis and should be especially helpful to one who is beginning work in this area. The chapters on reaction gas chromatography, accumulation methods, and methods of preparing calibration mixtures are particularly well done. The book provides a good access to the older (pre-1970) literature on gas chromatographic trace analysis and gives key references (through 1969) where detailed procedures for major methods of analysis can be found.

For one who is experienced in gas chromatographic trace analysis and is familiar with the literature, it is doubtful that the book would be of much practical value.

The main shortcoming of the book is that it does not represent the current state-of-the-art of gas chromatographic methods for trace analyses. Since publication of the original Russian text in 1970, significant technological advances have been made—particularly in the area of environmental analyses. Unfortunately, the current English translation does not include an updating of the literature. For example, the important role of capillary gas chromatographic methods in trace analysis is not discussed. Also missing are discussions of the recent major advances in the use of microcoulometric and flame-photometric detectors and combined gas chromatographic-mass spectrometer techniques. In column technology, there have been significant developments in methodology based on the use of newer types of column packings, such as porous polymers and supports with chemically bonded liquid phases. In the area of instrumentation, specialized gas chromatographic instrumentation is now available which enables trace analysis of many materials to be made rapidly, accurately, and automatically. These newer methods have supplemented or replaced many of the older gas chromatographic methods discussed in the book. Therefore, for optimum benefit from the book, the reader should supplement it with a current search of the literature.

D. K. Albert, *Amoco Oil Company*

Free Radicals. Volume 2. Edited by J. K. KOCHI (Indiana University). Wiley-Interscience, New York, N. Y. 1973. xx + 906 pp. \$42.50.

The second and last volume of the monograph includes the remaining three parts (in the review of Vol. 1, *J. Amer. Chem. Soc.*, **95**, 8493 (1973), *four volumes* should be replaced by *four parts*).

Part 2, Free Radical Chain Reactions, consists of chapters on homogeneous liquid-phase autoxidations (J. A. Howard), addition to multiple bonds (P. I. Abell), atom-transfer and substitution reactions, halogenation (M. L. Poutsna), and aromatic substitution (M. J. Perkins).

Part 3, "Structure and Energetics," consists of chapters on thermochemistry of free radicals (H. E. O'Neal and S. W. Benson), the structure and stereochemistry of free radicals (L. Kaplan), structure of free radicals by ESR spectroscopy (H. Fischer), and solvation and association (J. C. Martin).

Part 4, "Free Radicals with Heteroatoms," consists of chapters on nitrogen-centered radicals (S. F. Nelsen), phosphorus radicals (W. G. Bentrude), oxygen radicals (J. K. Kochi), sulfur-centered radicals (J. L. Kice), group IVB radicals (H. Sakurai), and bridged free radicals (P. S. Skell and K. J. Shea).

A subject index is appended. An author index would have been useful.