1,2-Bis(trimethylsilyl)ethane (16). Methyldichlorosilane (Alfa) (2.30 g, 20 mmol) and vinyldichlorosilane (Alfa) (2.82 g, 20 mmol) were catalyzed to combine using the usual H_2PtCl_6/*i*-PrOH catalyst. A vigorous reaction occurred, and the 5.1 g of product was combined without purification with excess methyl magnesium iodide in ether. After 3 hr reflux, the product was washed, dried, and distilled to give 97% yield of 1,2-bis(trimethylsilyl)ethane (**16**): bp 79° (68 Torr) (lit.[31] 151°); NMR 0.05 (s, 18 H), 0.41 (s, 4 H).

Acknowledgment. We are grateful to Dr. Gerald Koermer, Dr. David Eaton, and Mr. Michael Hall for preparing some of the compounds, to Dr. David Starks for one of the photoelectron spectra, and to the National Science Foundation for support.

References and Notes

(1) Supported by the National Science Foundation, Grant 38772X.
(2) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971).
(3) (a) H. Schmidt, A. Schweig, and G. Manuel, *J. Organomet. Chem.*, **55**, 1 (1973); (b) A. Schweig, U. Weidner, and G. Manuel, *ibid.*, **54**, 145 (1973), and references cited there.
(4) C. G. Pitt, *J. Organomet. Chem.*, **61**, 49 (1973).
(5) A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organomet. Chem.*, **20**, 49 (1969).
(6) (a) P. Bischof, R. Gleiter, E. Heilbronner, V. Hornung, and G. Schröder, *Helv. Chim. Acta*, **53**, 1645 (1970); (b) R. Gleiter, E. Heilbronner, and A. de Meijere, *ibid.*, **54**, 1029 (1971); (c) E. Heilbronner, R. Gleiter, T. Hoshi, and A. de Meijere, *ibid.*, **56**, 1594 (1973); (d) M. Beez, G. Bieri, H. Bock, and E. Heilbronner, *ibid.*, **56**, 1028 (1973).
(7) W. Hanstein and T. G. Traylor, *Tetrahedron Lett.*, 4451 (1967).
(8) A. Streitwieser, Jr., *Prog. Phys. Org. Chem.*, **1**, 1 (1963).
(9) (a) D. W. Turner, *Adv. Phys. Org. Chem.*, **4**, 31 (1966); (b) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, New York, N.Y., 1970.
(10) (a) V. F. Traven and R. West, *J. Am. Chem. Soc.*, **95**, 6824 (1973); (b) H. Sakurai, M. Kira, and T. Uchida, *ibid.*, **95**, 6826 (1973); (c) H. Bock and W. Ensslin, *Angew. Chem., Int. Ed. Engl.*, **10**, 404 (1971).
(11) N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Am. Chem. Soc.*, **92**, 19 (1970).
(12) W. R. Moore and C. R. Costin, *J. Am. Chem. Soc.*, **93**, 4910 (1971).
(13) R. S. Brown, D. F. Eaton, A. Hosomi, T. G. Traylor, and J. M. Wright, *J. Organomet. Chem.*, **64**, 249 (1974).
(14) (a) C. Eaborn, "Organosilicon Compounds", Academic Press, London, 1960, p 45; (b) R. C. Poller, "Chemistry of Organotin Compounds", Logos, Plainfield, N.J., 1970, p 107.
(15) S. Evans, A. F. Orchard, and D. W. Turner, *Int. J. Mass. Spectrom. Ion Phys.*, 7, 261 (1971).
(16) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92**, 7476 (1970).
(17) (a) S. Cradock and R. A. Whiteford, *J. Chem. Soc., Faraday Trans. 2*, **68**, 281 (1972); (b) T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **46**, 1558 (1973).
(18) (a) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971); (b) H. Bock and B. R. Ramsey, *Angew. Chem. Int. Ed. Engl.*, **12**, 743 (1973); (c) W. Kutzelnigy, *ibid.*, **12**, 546 (1973).
(19) D. Eaton (unpublished work) has measured the first ionization energy for bornyltrimethyltin of 8.52 eV.
(20) S. F. Nelson and J. M. Bushek, *J. Am. Chem. Soc.*, **95**, 2011 (1973).
(21) M. Rosenblum, *Acc. Chem. Res.*, **4**, 122 (1974).
(22) G. Hartman and T. G. Traylor, in press.
(23) Z. M. Manulkin, *J. Gen. Chem. USSR*, **13**, 46 (1943).
(24) R. H. Bullard and A. C. Haussman, *J. Phys. Chem.*, **34**, 743 (1930).
(25) C. F. Shaw, III, and A. L. Allred, *J. Organomet. Chem.*, **28**, 53 (1971).
(26) J. Jerkunica and T. G. Traylor, *J. Am. Chem. Soc.*, **93**, 6278 (1971).
(27) T. G. Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, **30**, 599 (1972).
(28) G. Koermer, unpublished work.
(29) M. M. Koton, T. M. Kiseleva, and N. P. Zapevalova, *Zh. Obshch. Khim.*, **30**, 186 (1960).
(30) T. T. Tidwell and T. G. Traylor, *J. Org. Chem.*, **33**, 2614 (1968).
(31) D. N. Andreev and E. V. Kukharskaya, *Dokl. Akad. Nauk SSSR*, **134**, 89 (1960).

An ab Initio Study of Acyloxy Cations

Wilhelm F. Maier* and Manfred T. Reetz*[1]

Contribution from the Department of Chemistry, University of California,
Berkeley, California 94720, and Fachbereich Chemie der Philipps-Universität,
3550 Marburg, Lahnberge, West Germany. *Received August 26, 1974*

Abstract: The geometry, electronic structure, and energy of several acyloxy cations (I) have been determined by ab initio self-consistent field calculations with minimum and double ζ basis sets. The optimized structures show the isomeric cyclic dioxiryl cation (II) to be the lowest energy species. Substituent effects on the decomposition energy of II yielding cations III and carbon dioxide have been examined.

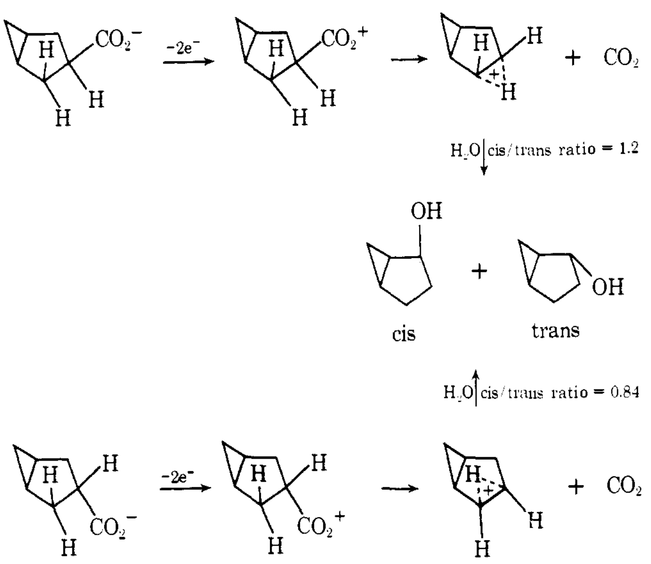
Although many semiempirical and ab initio molecular orbital calculations on carbocations are known, little work on organic cations in which heteroatoms bear the positive charge has been reported to date.[2] In this paper we present the results of an ab initio study of acyloxy cations RCO_2^+. These calculations were performed with the aim of obtaining information of such species in advance of experimental work. Acyloxy cations have been discussed occasionally as possible reactive intermediates in side reactions of the Kolbe electrolysis leading to carbenium ion-derived products, but no consensus regarding their existence has been reached to date.[3] For example, the partial stereospecificity observed in the electrolysis of *cis*- and *trans*-bicyclo[3.1.0]hexane-3-carboxylic acid was cited by Gassman[4] as evidence for the intermediacy of RCO_2^+ ions (Scheme I).

Acyloxy cations have also been invoked in the anodic oxidation of isomeric 3-methyl-2-phenylcyclopropanecarboxylic acids.[5] In analogy to the well-known solvolysis of cyclopropyl halides and tosylates,[6] carbon dioxide evolution with concomitant disrotatory electrocyclic ring opening was assumed (Scheme II). The role of intermediate acyloxy cations in the electrolysis of cyclopropanecarboxylic acids has since been questioned.[7] Similarly, Skell[8] has presented evidence against the formation of RCO_2^+ in the electrolytic oxidation of aliphatic carboxylic acids.

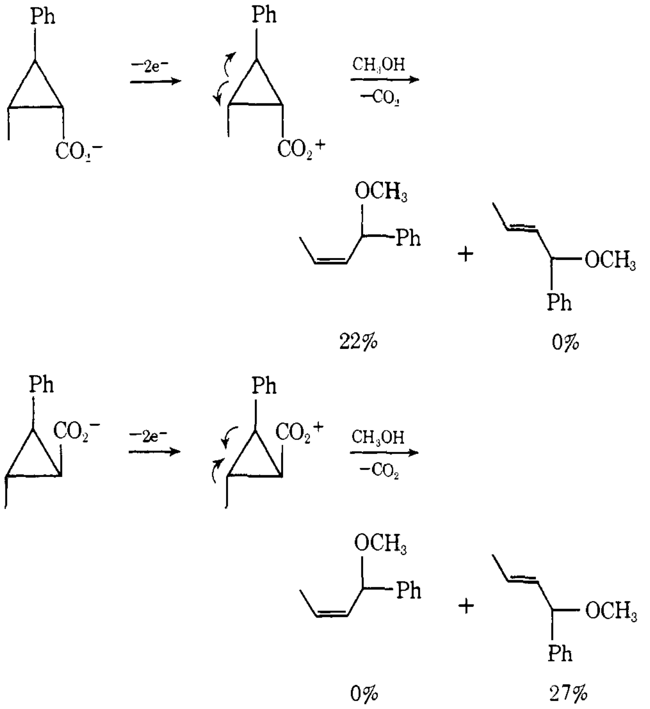
Acyloxy cations have also been postulated to occur in chemical oxidations. Thus, Mosher and Kehr[9] prefer an ionic mechanism for the lead(IV) induced oxidation of carboxylic acids (Scheme III). It should be noted that in *nonpolar* media a radical mechanism has been shown to be operating.[10]

In the references cited above, neither the geometry nor the possible electronic structure of acyloxy cations was considered. Our initial investigation[11] of these species with semiempirical SCF-MO calculations at the MINDO/2[12] level resulted in a potential energy surface which shows a pronounced energy gain in going from the acyloxy cation I (R = H) to the isomeric dioxiryl cation II (Scheme IV). The latter species had not been mentioned previously in the literature.

Scheme I



Scheme II

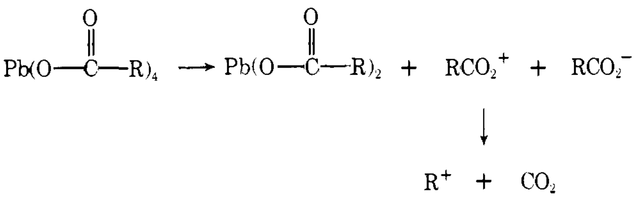


Additional MINDO/2 calculations on II having various substituents (R = methyl, phenyl, cyclopropyl) showed surprisingly high stability as indicated by heats of formation.[11] These studies have now been extended with ab initio calculations. Particular emphasis has been placed on the energy of I and II as a function of the substituent (R), and on the possible decomposition leading to cations III and carbon dioxide (Scheme IV).

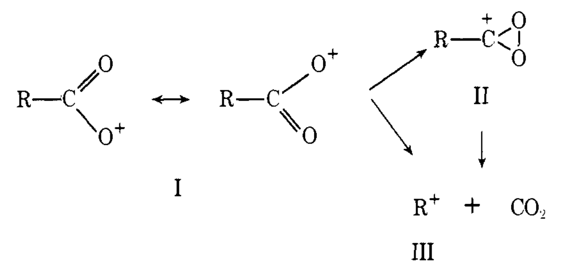
Methods and Results

The ab initio SCF-MO calculations were carried out with the highly efficient GAUSSIAN-70 program.[13] A wide range of calculations are available from previous application of this program by the Pople group.[14] The success and low computer time of this method prompted us to apply it in our investigation. We employed the STO-3G minimal basis set with a least-squares fit of three gaussians per Slater orbital[15] and the 4-31G extended basis set in which two functions are used for each valence orbital.[16]

Scheme III



Scheme IV



Exploratory calculations were performed on the parent molecule HCO_2^+, because it is small and reflects the electronic properties of the CO_2^+ group without the influence of substituents. The geometry was optimized first with MINDO/2[11] and then with the STO-3G basis set. Both methods lead to the conclusion that the optimized geometry corresponds to the cyclic form II (R = H) rather than to the acyloxy isomer I (R = H). However, substantial differences in bond lengths and angles were obtained. In order to shed light on this surprising discrepancy, further optimization with the 4-31G basis set was carried out. The results, summarized in Table I, show that the STO-3G and 4-31G basis sets lead to similar geometries, although the latter points to a somewhat longer O-O bond distance.

The orbital energies (4-31G) of optimized II (R = H) and of I (R = H) constrained to the geometry of formate anion[17] are shown in Table II. The lowest unoccupied MO in HCO_2^+ with structure I has b_2 symmetry. It is a σ MO, antibonding between the oxygen atoms. In the anion HCO_2^- this MO is occupied and leads to a preference for the noncyclic geometry. The geometric change in HCO_2^+ leading from I to II produces an energy decrease in all of the O-O symmetrical orbitals (a_1, b_1) and an energy increase in all of the O-O antisymmetric orbitals (a_2, b_2). Since all of the orbitals remain occupied, this process is thermally allowed by orbital symmetry[18] (Figure 1). The ground state of HCO_2^+ (II) is $^1A_2$ with the configuration:

$$1a_1^2 1b_2^2 2a_1^2 3a_1^2 2b_2^2 4a_1^2 5a_1^2 1b_1^2 3b_2^2 6a_1^2 1a_2^2$$

Noteworthy is also the pronounced difference in energy separation between the highest occupied and the lowest unoccupied MO's in I and II (Table II).

The total energies of I and II are given in Table III. According to the STO-3G and 4-31G calculations, the transformation of I to II is accompanied by an energy gain of 81.4 kcal/mol and 48.1 kcal/mol, respectively. In general, MINDO/2[19] and STO-36[20] tend to favor small rings, as shown by isomerization energies. This artifact is reflected in the short O-O bond distance of the optimized structure and in the energy difference between I and II. In contrast, the 4-31G calculations lead to a longer optimized O-O bond length and to a smaller isomerization energy. It should be pointed out that in the study of small rings the 4-31G basis set provides a more reliable tool in energy comparisons.[20]

In evaluating the electronic properties of the two isomeric forms, it is interesting to note that I has more *oxenium* ion

Table I. Optimized Equilibrium Geometries of HCO_2^+ (Å)

	MINDO/2	STO-3G	4-31G
O–O	1.329	1.515	1.650
C–O	1.290	1.334	1.301
C–H	(1.09)[a]	1.13	(1.13)[a]

[a] Not optimized.

Table II. Orbital Energies (hartrees) of HCO_2^+ (4-31G Basis)

I			II
−0.222	b_1	b_2	−0.204
−0.481	b_2	b_1	−0.280
−0.792	a_1	a_2	−0.846
−0.916	a_2	a_1	−0.917
−1.038	b_1	b_2	−0.957
−1.057	b_2	b_1	−1.051
−1.080	a_1	a_1	−1.082
−1.223	a_1	a_1	−1.256
−1.774	b_2	b_2	−1.599
−1.887	a_1	a_1	−1.996
−11.792	a_1	a_1	−11.829
−21.065	a_1	b_2	−21.026
−21.065	b_2	a_1	−21.027

Table III. Total Energies (hartrees) of HCO_2^+

	I	II
STO-3G	−185.102	−185.231
4-31G	−187.249	−187.325

character than II. The calculated electron population shows that the electron density at the oxygen atoms increases as the electrocyclic ring closure proceeds from I to II, as summarized in Table IV. The transformation thus brings about the expected increase in positive charge at the carbon atom.

The increasing carbenium ion character suggests the possibility of stabilizing II by electron donating substituents. Fluorine, methyl, and ethinyl were tested. The minimal basis set was used in order to demonstrate the qualitative effect of substituents on the CO_2^+ group. This approach was not expected to yield highly reliable quantitative data, however. The effect of substitution on the geometry of the ring in II was first considered. In case of an important dependence of ring geometry on the nature of the substituent, of all groups studied, fluorine should show one of the largest effects. The optimized geometry of II (R = F) was found to be: F-C, 1.274 Å; C-O, 1.343 Å; O-O, 1.515 Å. Evidently fluorine has no appreciable influence on the geometry. We therefore used the HCO_2^+ geometry for all additional substituents without further optimization.

The STO-3G orbital population derived from a Mulliken population analysis[21] shows that fluorine *decreases* the electron density at the carbon atom of II, the π-donor effect being apparent only at the oxygen atoms (Table V). The π population at the carbon is raised, but the σ-acceptor ability of fluorine dominates. Table VI gives the charge distribution derived from atom population in the substituted dioxiryl cations. Noteworthy is the electron releasing effect of the methyl group, as evidenced by the positive charge of 0.2 per hydrogen atom. However, almost no change occurs in the π system, the effect being predominantly one of σ donation. In the case of R = ethinyl the main electronic change occurs in the π system of the CO_2^+ segment.

The substituent effect on the isomerization and decomposition energies was also examined with the STO-3G basis (Table VII). Fluorine does not lead to the initially expected effect. The other substituents likewise fail to cause drastic changes in the energy of II relative to I. The most efficient group in this respect appears to be ethinyl, which brings about a gain of 99.9 kcal/mol in going from I to II, compared to a value of 81.5 kcal/mol for the unsubstituted cations. The effect of the methyl group is less than anticipated, i.e., the isomerization energy increases by only 4.6 kcal/mol upon substitution.

Table IV. Electron Population (electrons/atom) in HCO_2^+

	I		II	
	4-31G	STO-3G	4-31G	STO-3G
C	5.32	5.67	5.10	5.52
O	8.02	7.87	8.19	7.91

Table V. Orbital Population (electrons/orbital) in II

		R =	
		H	F
O	2p	1.767	1.810
C	2p	0.465	0.588
C	2s	1.203	1.060

Table VI. Charge Distribution in II

	R =			
	H	F	CH_3	HC≡C
C	+0.40	+0.70	+0.52	+0.50
O	+0.10	+0.09	+0.06	+0.06
R	+0.32	+0.21	−0.21 (C) +0.20 (H)	+0.38 (αC)

Table VII. Energetics of RCO_2^+

Method	R	Total energy of II, hartrees	Isomerization I → II, kcal/mol	Decomposition[c] II → III + CO_2, kcal/mol
STO-3G	H	−185.231	−48.6	+107.0
STO-3G	F	−282.691	−79.4	+6.5
STO-3G	CH_3[a]	−223.798	−86.1	−28.4
STO-3G	HC≡C[b]	−259.997	−99.9	+34.0
4-31G	H	−187.325	−48.6	−1.8
4-31G	F	−286.017		+4.2
4-31G	CH_3[a]	−226.303		−123.3

[a] For the CH_3C^+ segment the STO-3G optimized geometry of $CH_3CH_2^+$ was used as given by W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.*, 93, 808 (1971). [b] Experimental geometry was used: *Chem. Soc., Spec. Publ.*, No. 11 (1958). [c] Energies of the optimized cations (R^+) and CO_2 were used as calculated previously.[15]

An important aspect regarding the feasibility of generating RCO_2^+ ions experimentally concerns their possible decomposition into R^+ (III) and carbon dioxide. Such a reaction might be expected to be thermodynamically favored, particularly if III is a stable ion. In order to explore this possibility, the difference in total energy between II and the decomposition products was calculated for several substituted ions using the minimal basis set. The values scatter widely according to the nature of the substituent (Table VII). The methyl derivative appears to be the only member of the series which decomposes exothermically. The parent ion HCO_2^+ occupies the other extreme, its resistance to decomposition being unexpectantly high. The decomposition energies of several of the II ions were therefore recalculated using the more reliable extended basis set (Table VII). The results show that decomposition of the fluorine derivative is slightly endothermic by 4.2 kcal/mol. Carbon dioxide evolution in the case of the parent ion (II, R = H) is nearly thermoneutral. In contrast, decomposition of the methyl derivative is highly exothermic, bringing about an energy gain of 123.3 kcal/mol. Although the decomposition does not belong to any of the classes of pericyclic reactions as delin-

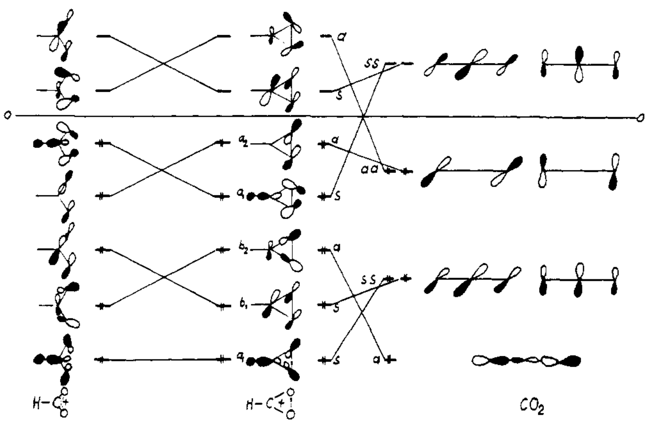


Figure 1. Correlation diagram for ring closure and decomposition.

eated by Woodward and Hoffmann, it is nevertheless thermally forbidden by orbital symmetry. The highest occupied a_1 MO of II correlates with one of the antibonding orbitals of carbon dioxide. Figure 1 shows the relevant orbitals. H^+ can be omitted since it is unoccupied. On the basis of this symmetry restriction an energy barrier to decomposition is to be expected.

Two additional calculations with the 4-31G extended basis set were performed on $CH_3CO_2^+$ and FCO_2^+ with the purpose of testing the validity of the substituent effects derived from the minimal basis set. These show that the relative stability of $CH_3CO_2^+$ and HCO_2^+ with respect to decomposition is similar to that obtained previously by STO-3G. In contrast, a dramatic change is noted for the fluorine derivative, which is now calculated to be more stable than HCO_2^+. The results indicate that the qualitative details of the electronic effects of substituents are reproduced quite well with the minimal basis set (Table VII). It is probably somewhat unreliable with respect to the relative magnitudes of stabilization, however. Here the 4-31G basis is better suited. The inner and outer flexibility of the valence shell orbitals of the 4-31G basis makes this set a useful tool for investigating substituent effects, as noted previously in a study of bond separation and hydrogenation energies.[22]

Conclusion

The immediate result of this study relates to the high stability of dioxiryl cations (II) relative to the acyloxy isomers (I), a conclusion previously reached on the basis of MINDO/2 calculations.[11] For the parent cations (R = H) the 4-31G extended basis set gives an isomerization energy of 48.6 kcal/mol. Thus, any attempted generation of I may in fact lead to II. The calculations also show that the isomerization energy does not vary significantly according to the nature of the substituent. In contrast, a different pattern of substituent effects is observed for the molecular decomposition of RCO_2^+ yielding R^+ and carbon dioxide. The energetics of this reaction depends very much on the type of substitution. This behavior is easily traced to the relative stability of the liberated cation. According to both basis sets the most stable cation studied, CH_3^+, is formed exothermically. It is reasonable to expect an even higher exothermicity for more stable ions such as ethyl or other alkyl derivatives. Different chemical behavior may prevail if the product ion is highly unstable, such as in the decomposition of FCO_2^+. In any case, some degree of kinetic stability may be expected due to the forbiddeness of the reaction.

We conclude that dioxiryl cations (II) *may* be intermediates on the potential energy surface of oxidative decarboxylations leading from carboxylate anions to carbenium ion products. The chemistry postulated for acyloxy cations can equally well be expected of the cyclic dioxiryl form. Thus the stereospecificity of the processes in which acyloxy cations (I) have been invoked[3-5] is also explained by the intermediacy of the isomeric dioxiryl cations. Similar arguments can be construed for the lead(IV) oxidation of carboxylic acids.[9]

We are currently expanding our investigation to include other heteroallylic systems such as RCN_2^+ and $RC(NH)_2^+$.

Acknowledgment. This work was carried out with the generous support of Professors A. Streitwieser, Jr., and D. Shirley. We especially thank Professor Streitwieser and Dr. J. McKelvey for many helpful discussions and instructions and for the use of their GAUSSIAN-70 version. The ab initio calculations were performed at the computer center of the University of California, Berkeley.

References and Notes

(1) Address correspondence to either author at Fachbereich Chemie der Philipps-Universität.
(2) For nonempirical SCF calculations on NH_2^+, see S. Y. Chu, A. K. Q. Siu, and E. F. Hayes, *J. Am. Chem. Soc.*, **94**, 2969 (1972); J. F. Harrison and C. W. Eakers, *ibid.*, **95**, 3467 (1973).
(3) Recent reviews: L. Eberson and H. Schäfer, *Fortschr. Chem. Forsch.*, **21**, 1 (1971); L. Eberson In "Organic Electrochemistry", M. M. Baizer, Ed., Marcel Dekker, New York, N.Y., 1973; A. K. Vijh and B. E. Conway, *Chem. Rev.*, **6**, 623 (1967).
(4) P. G. Gassman and F. V. Zalar, *J. Am. Chem. Soc.*, **88**, 2252 (1966).
(5) T. Shono, I. Nishiguchi, S. Yamane, and R. Oda, *Tetrahedron Lett.*, 1965 (1969).
(6) Recent review: P. v. R. Schleyer, W. F. Sliwinski, G. W. van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *J. Am. Chem. Soc.*, **94**, 125 (1972).
(7) L. B. Rodewald and M. C. Lewis, *Tetrahedron*, **27**, 5273 (1971).
(8) P. H. Reichenbacher, M. D. Morris, and P. S. Skell, *J. Am. Chem. Soc.*, **90**, 3432 (1968).
(9) W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953); see also E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963); W. H. Starnes, Jr., *ibid.*, **86**, 5603 (1964).
(10) J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 3609 (1965).
(11) M. T. Reetz and W. F. Maier, *Theor. Chim. Acta*, **35**, 163 (1974).
(12) M. J. S. Dewar and E. Haselbach, *J. Am. Chem. Soc.*, **92**, 590 (1970).
(13) QCPE program No. 236.
(14) W. A. Lathan, L. A. Curtiss, W. J.Hehre, J. B. Lisle, and J. A. Pople, *Progr. Phys. Org. Chem.*, **11**, 175 (1974).
(15) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(16) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1970).
(17) An OCO bond angle of 124° was used, corresponding to the experimental value: W. H. Zachariasen, *J. Am. Chem. Soc.*, **62**, 1011 (1940).
(18) R. B. Woodward and R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, **8**, 781 (1969).
(19) M. J. S. Dewar, *Fortschr. Chem. Forsch.*, **23**, 1 (1971).
(20) L. Radom, W. A. Lathan, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 5341 (1971).
(21) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(22) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).