rotation about the C–O axis. Both of these factors should result in a substantial lowering of the normal prohibition to spin interconversion in a concerted reaction and thereby rationalize the astoundingly high yield of A_3 produced when **1** fragments! The diabatic nature (change from a ground to excited state surface) of the process is probably further facilitated by the similarity of $\mathbf{1}^{\neq}$ to $(A_* + A_0)$ in energetics, electronic structure (Figure 1), and nuclear structure (r_{CO} of $A_* \sim 1.32$ Å, r_{CO} of $\mathbf{1} \sim 1.42$ Å).[12b] In addition, the concerted model explains (a) the low, even negative values of $\Delta S^{\neq}$ for decomposition of **1** and other dioxetanes in nonpolar solvents as being due to the low probability that the proper vibrations[14] needed to achieve $\mathbf{1}^{\neq}$ will be found, even when the molecule has achieved sufficient activation energy;[14b] (b) the lack of structural effects as being due to a leading O–O rupture in achieving $\mathbf{1}^{\neq}$; and (c) the failure of a rate enchancement in acetonitrile as compensating ground- and transition-state stabilization, while methanol provides specific *transition state* stabilization, due to hydrogen bonding of the fragmenting O–O bond.

The driving force for favored triplet formation when **1** thermolyzes is probably the much lower energy of triplet **1** relative to singlet **1**, which causes a prior intersection of the ground-state energy surface of **1** and triplet energy surfaces leading to products. This conclusion finds strong corroboration in the theoretical analysis of 1,2-dioxetane decompositions reported by Kearns.[15]

To the best of our knowledge, this report represents one of the few attempts to apply the formalism of a spin–orbital coupling operator to assist in the understanding of a unimolecular chemical reaction of an organic molecule.[16] We feel that the success of such a treatment should encourage further consideration of the use of the ideas on radiationless processes between electronic states long employed by molecular spectroscopists,[3] to analyze certain chemical reactions, especially those involving generation of organic molecules in electronically excited states.

Acknowledgments. We are grateful to Drs. A. A. Lamola, W. H. Richardson, L. Salem, and K. Müller for very informative and stimulating discussions of the ideas presented in this paper.

---

(14) (a) Indeed, the activation parameters for decomposition of the three methylated 1,2-dioxetanes listed in Table I bear a striking resemblance to those for a classical pericyclic reaction, the ring opening of cyclobutenes to butadienes. For pertinent data see M. R. Willcott, R. L. Cargill, and A. B. Sears, *Progr. Phys. Org. Chem.*, **9**, 1 (1972). (b) The biradical mechanism can be maintained if one is willing to suppose that the solvent effects are ambiguous, the alkoxy model is a poor one, or that the triplet biradical has a much greater tendency to form products than the singlet biradical (which closes reversibly). Thus, the two mechanisms may be very similar in terms of predicting experimental response to various changes in structure and reaction conditions. However, we feel that some unusual observations, such as the tremendous stability of a bisadamantyldioxetane (J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972)), can be explained nicely on the basis of inhibition of the lowest energy vibronic motions for cleaving the O–O bond of the dioxetane.

(15) D. Kearns, *Chem. Rev.*, 71, 395 (1971).

(16) For recent theoretical studies of radiationless processes see R. G. Gilbert and I. G. Ross, *Austr. J. Chem.*, **24**, 1541 (1971); T. Y. Chang and H. Basch, *Chem. Phys. Lett.*, **5**, 147 (1970).

(17) NATO Fellow, 1971–1972.

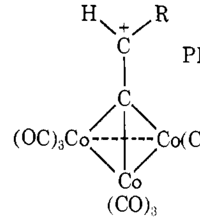
Nicholas J. Turro,* Peter Lechtken[17]
Department of Chemistry, Columbia University
New York, New York 10027

Received July 5, 1972

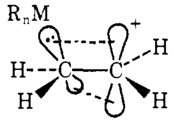
Organocobalt Cluster Complexes. XI. Carbonium Ion Derivatives[1]

Sir:

The stabilization of π-complexed carbonium ions in transition metal complexes is by now a well-known phenomenon,[2] but the stabilization of carbonium ions in σ-bonded organotransition metal structures is implied by only a few examples.[3] We report here concerning three novel carbonium ion salts, I, II, and III,



I, R = H
II, R = CH_3
III, R = C_6H_5

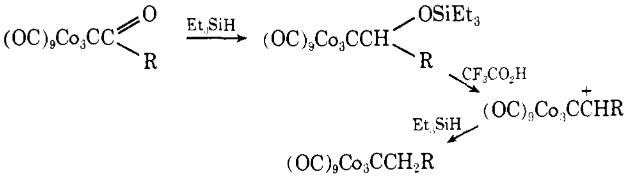


IV

whose stability we believe to be a direct consequence of their position relative to the three cobalt atoms in the cluster.

During the course of our studies dealing with carbon-functional alkylidynetricobalt nonacarbonyl complexes,[1,4] we studied the reduction of acyl derivatives, $(OC)_9Co_3CC(O)R$.[1] Their direct reduction to the alkyls, $(OC)_9Co_3CCH_2R$, by the action of triethylsilane and trifluoroacetic acid in THF solution proved to be a facile, high-yield process and this suggested to us that the cluster carbonium ions were readily accessible and possibly quite stable (Scheme I). The reaction course shown implies that it is the presence of the trifluoroacetic acid which is responsible for the reduction to the alkyl derivative. If this is so, then reduction of acyl derivatives to the corresponding alcohols might be possible if the acid were omitted. Such was the case. Reaction of the $(OC)_9Co_3CC(O)R$ (R = H, CH_3, C_6H_5) with equimolar quantities of Et_3SiH in refluxing benzene under an atmosphere of carbon monoxide gave (after treatment of the mixture with concentrated H_2SO_4 and then with ice water) the expected alcohols: $(OC)_9Co_3CCH(OH)R$ (R = H, mp 161–163°, 46%; R = CH_3, mp 158–160°, 88%; R = Ph, mp 87–89°, 68%). These proved to be useful starting materials for the preparation of I, II, and III.[5]

Scheme I



---

(1) Part X: D. Seyferth and J. E. Hallgren, *J. Organometal. Chem.*, in press.

(2) M. L. H. Green in G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, 3rd ed, Methuen & Co., London, 1968.

(3) Reference 2, Chapter 7, especially pp 209–217.

(4) (a) D. Seyferth and A. T. Wehman, *J. Amer. Chem. Soc.*, **92**, 237 (1970); (b) J. E. Hallgren, C. S. Eschbach, and D. Seyferth, *ibid.*, **94**, 2547 (1972); (c) D. Seyferth and G. H. Williams, *J. Organometal. Chem.*, **38**, C11 (1972); (d) D. Seyferth, J. E. Hallgren, and P. L. K. Hung, *ibid.*, in press.

(5) Previous workers were unable to prepare such alcohols by direct reaction of $Co_2(CO)_8$ with $CX_3CRR'OH$ (X = Cl, Br; R, R' = H, H; H, Me; Me, Me): G. Pâlyi, F. Piacenti, M. Bianchi, and E. Benedetti, *Acta Chim. Sci. Hung.*, **66**, 127 (1970).

Table I. Organocobalt Cluster Derivatives Prepared from the Carbonium Ion Hexafluorophosphates

R in $(OC)_9Co_3$-CC^+HR	Reactant	Product (% yield)	Mp, °C
H	MeOH	$(OC)_9Co_3CCH_2OMe$ (85)	128–129
H	EtOH	$(OC)_9Co_3CCH_2OEt$ (76)	54–56
H	$PhNH_2$	$(OC)_9Co_3CCH_2NHPh$ (67)	69–71
H	$C_6H_5NMe_2$	$(OC)_9Co_3CCH_2C_6H_4NMe_2$-*p* (49)	Unstable
Me	MeOH	$(OC)_9Co_3CCH(Me)OMe$ (85)	176–177
Me	EtOH	$(OC)_9Co_3CCH(Me)OEt$ (82)	61–63d
Me	PhSH	$(OC)_9Co_3CCH(Me)SPh$ (42)	73–75
Me	$PhNH_2$	$(OC)_9Co_3CCH(Me)NHPh$ (73)	117–119
Me	$C_6H_5NMe_2$	$(OC)_9Co_3CCH{=}CH_2$ (68)	144–146
Ph	MeOH	$(OC)_9Co_3CCH(Ph)OMe$ (59)	70–72
Ph	EtOH	$(OC)_9Co_3CCH(Ph)OEt$ (75)	77–79
Ph	PhSH	$(OC)_9Co_3CCH(Ph)SPh$ (38)	93–95
Ph	$PhNH_2$	$(OC)_9Co_3CCH(Ph)NHPh$ (59)	126–127
Ph	$C_6H_5NMe_2$	$(OC)_9Co_3CCH(Ph)C_6H_4NMe_2$-*p* (54)	101–103

Treatment of 1.5 mmol of $(OC)_9Co_3CCH(OH)CH_3$ in propionic anhydride solution with 2 mmol of 65% aqueous HPF_6 under nitrogen resulted in precipitation of a black solid. The latter was washed with dichloromethane and dried *in vacuo* (Schlenk apparatus). The resulting black, microcrystalline solid gave the correct analytical values for II. *Anal.* Calcd for $C_{12}H_4O_9F_6PCo_3$: C, 23.48; H, 0.66; F, 18.57; Co, 28.80. Found: C, 23.45; H, 0.74; F, 18.79; Co, 29.39.

Analytically pure samples of I and III were prepared in a similar manner. These salts were quite stable in the absence of air and moisture. Initial results of our study of their reactions (with alcohols, a thiol, aniline, and *N*,*N*-dimethylaniline) are presented in Table I. Reactions were carried out under nitrogen either by adding the reactant to the solid PF_6^- salt or to its suspension in well-dried benzene. The products were purified by column chromatography and/or sublimation *in vacuo*. All were characterized by their ir and nmr spectra and by combustion analysis.

In agreement with the postulated reaction course in Scheme I, the reaction of $(OC)_9Co_3CCH(OH)CH_3$ with equimolar quantities of triethylsilane and trifluoroacetic acid, in THF at reflux, resulted in reduction to $(OC)_9Co_3CCH_2CH_3$ in 72% yield.

From these results it would appear that carbonium ions I, II, and III are readily formed and quite stable. Especially noteworthy is the ready accessibility of the primary carbonium ion, I. We suggest that the structure of these carbonium ions presents an especially favorable opportunity for σ–π stabilization. It has been recognized that organometallic substituents in the β position greatly stabilize carbonium ion centers *via* σ–π conjugation (IV).[6] In the cobalt cluster carbonium ions, I, II, and II, such σ–π stabilization should make substantial contribution to their stability. Rotation about the exocluster C–C bond presents three opportunities for such lateral σ–π overlap. In this connection, the easy accessibility of the acylium ion, $(OC)_9Co_3CC^+O$,[4b,c] is to be noted. Here also a contribution from such σ–π conjugation may be discussed.

We are continuing this investigation with further preparative studies and with more quantitative studies which we hope will provide information concerning the stability of these carbonium ions relative to other stabilized carbonium ion species.

Acknowledgments. The authors are grateful to the National Science Foundation for generous support of this research (NSF Grant No. GP-31429X).

Dietmar Seyferth,* Gary H. Williams, John E. Hallgren
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received October 7, 1972

---

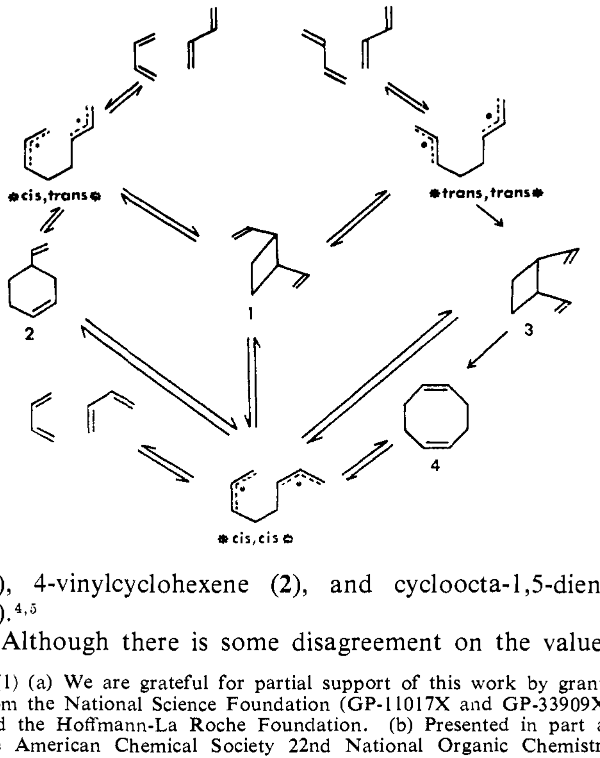
[6] T. G. Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, 30, 599 (1972).

Rearrangement of *trans*-1,2-Divinylcyclobutane and the Energy Surface of the Dimers of Butadiene[1]

Sir:

In many thermal reactions, the experimentally determined heat of formation ($\Delta H_f°$) of the transition state is that predicted by bond additivity data to be appropriate for a species with one broken bond, a "diradical."[2,3] From the logical converse of this correspondence, a procedure has developed for estimation of $\Delta H_f°$ of a hypothetical diradical intermediate in a given reaction by measurement of the activation energy of a different reaction assumed to pass through the "same" intermediate. A recent important application has concerned the energy surface common to the dimers of butadiene, in which values of $\Delta H_f°$ for the hypothetical octa-1,7-diene-3,6-diyl diradicals *trans,trans*, *cis,-trans*, and *cis,cis* were estimated from various pyrolysis reactions (Scheme I) of *trans*-1,2-divinylcyclobutane (1), 4-vinylcyclohexene (2), and cycloocta-1,5-diene (4).[4,5]

Scheme I



Although there is some disagreement on the values

---

[1] (a) We are grateful for partial support of this work by grants from the National Science Foundation (GP-11017X and GP-33909X) and the Hoffmann-La Roche Foundation. (b) Presented in part at the American Chemical Society 22nd National Organic Chemistry Symposium, Ann Arbor, Mich., June 1971, Abstracts, p 28.

[2] (a) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, 72, 1866 (1968); (b) *J. Chem. Eng. Data*, 15, 266 (1970); (c) *Int. J. Kinet.*, 2, 423 (1970); (d) S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," National Standard Data Reference Series NBS 21, U. S. Government Printing Office, Washington, D. C., 1970.

[3] H. M. Frey and R. Walsh, *Chem. Rev.*, 69, 103 (1969).