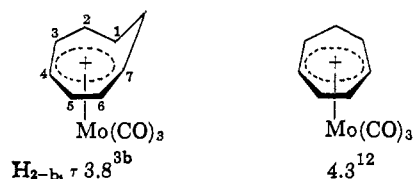


	I	V	VI
λ_{max} , m μ	232.5, 313	217, 273.5 ⁷	
$\log \epsilon$	4.52, 3.48	4.61, 3.63 ⁷	
H_{2-8} , τ	1.5 ⁹	1.0 ¹²	

of the nmr spectrum of I. Thus, the chemical shift of protons H_{2-8} in I is very similar to the value for H_{1-7} in tropylium ion.^{12,13} Further, the chemical shift between "inside" and "outside" C_8 protons in the monohomotropylium ion is well accounted for by a ring-current model using a 1.6-Å ring radius and a six-electron induced ring current. Using Framework Molecular Models^{14a} to estimate distances and the equation of Johnson and Bovey^{14b} to calculate chemical shifts due to induced ring currents, one obtains 5–6 ppm for the difference between inside and outside C_8 protons. This agrees well with the observed³ difference of 5.8 ppm.¹⁵

(12) H. J. Dauben, private communication; L. R. Honnen, Ph.D. Thesis, University of Washington, 1962; chemical shifts are in H_2SO_4 solvent.

(13) The same similarity of nmr chemical shifts of H_{2-8} in I and H_{1-7} in V is observed also with the corresponding $Mo(CO)_3$ complexes.



H_{2-8} , τ 3.8^{3b}

4.3¹²

(14) (a) Framework Molecular Orbital Models, Prentice Hall, Inc., Englewood Cliffs, N. J.; (b) C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

(15) NOTE ADDED IN PROOF. Just as the present manuscript was submitted, two pertinent communications by C. E. Keller and R. Pettit appeared (*J. Am. Chem. Soc.*, **88**, 604, 606 (1966)). In the first one, these authors report coupling constants for $C_8H_9^+$ essentially identical with those we reported earlier.^{3b} Also, they report that the protonation of methyl- and phenylcyclooctatetraene is structurally specific, the 1-substituted monohomotropylium ions being generated. As regards stereospecificity of these protonations in D_2SO_4 , these authors observed stereospecificity identical in direction and similar in magnitude with that we report here for the unsubstituted $C_8H_9^+$. For this latter protonation of the unsubstituted cyclooctatetraene in D_2SO_4 , Keller and Pettit still refer to the older report^{3a} of nonstereospecific protonation, apparently still unaware of the "inside-outside" equilibration. This may be an indication that such equilibration is slower with the substituted ions than with $C_8H_9^+$ itself.

In the second communication, Keller and Pettit object, as we did previously,^{3b} to Deno's representation of the monohomotropylium ion with a conventional cyclopropane ring (N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 148 (1964)). They also deal further with the question of a ring current in $C_8H_9^+$. For a series of related structures, with relatively constant geometry, in which the chemical shifts (δ) of the "inside" and "outside" protons vary only because of ring currents, one predicts from the Johnson-Bovey equation^{14b} that δ of the inside proton and δ of the outside one should each vary linearly with the chemical shift difference (Δ) between the two protons, Δ being a measure of the magnitude of the ring current. For seven systems plotted this way, roughly linear plots were observed for inside δ vs. Δ and outside δ vs. Δ . However, these roughly linear plots are fortuitous and misleading, since ring currents are not the only factor causing variation in δ . Variation of the charge at C_8 is also an important factor.

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Cholesteryl Perchlorate from Carbonium Perchlorate Ion-Pair Return^{1,2}

Sir:

In the course of further examination of the $HClO_4$ -catalyzed isomerization of *i*-cholesteryl acetate^{3a} I (*i*-ROAc) in acetic acid solvent to the thermodynamically favored cholesteryl isomer II (ROAc), we have observed a very instructive example of ion-pair return involving carbonium perchlorate ion pairs. This is described and discussed in the present communication.

The kinetics of the $HClO_4$ -catalyzed isomerization of *i*-ROAc to ROAc, followed polarimetrically, do not obey eq 1 for a reaction first order in added $HClO_4$ ($\Sigma HClO_4$), and also first order in *i*-ROAc. As illustrated in Table I, the k_2 values drift upwards badly

Table I. Summary of Kinetic Results at 25.0°

(<i>i</i> -ROAc), 10 ² M	($\Sigma HClO_4$), 10 ⁴ M	k_2 , l. mole ⁻¹ sec ⁻¹	10 ³ k_1 , sec ⁻¹
1.99	0.44	3.7–4.1	2.9
2.00	1.19	1.5–3.4	3.0
2.05	3.36	1.4–3.7	2.9
2.02	4.48	1.4–4.0	2.9
0.51	1.19	6.9–15.2	2.8
0.96	1.19	2.1–11.3	2.9
2.00	1.19	1.5–3.4	3.0
2.67	1.19	0.6–2.7	3.0

in each run and vary widely from run to run. While the isomerization is indeed first order in $\Sigma HClO_4$, it appears to be zero order⁴ in *i*-ROAc, eq 2 providing a good fit of all the data (Table I).

$$\text{rate} = k_2(i\text{-ROAc})(\Sigma HClO_4) \quad (1)$$

$$\text{rate} = k_1(\Sigma HClO_4) \quad (2)$$

The explanation which occurred to us for the peculiar kinetics of isomerization of excess *i*-ROAc by $HClO_4$ is that these two materials tend to be in steady-state equilibrium with a covalent perchlorate, chiefly cholesteryl perchlorate (IV, $ROClO_3$), during the isomerization (eq 3–5). This keeps the prevailing $HClO_4$ concentration during a kinetic run down to a small fraction of the added $\Sigma HClO_4$ and inversely proportional to the (*i*-ROAc), while ($ROClO_3$) is essentially equal to ($\Sigma HClO_4$). The kinetics of isomerization of *i*-ROAc are formulated with the aid of the carbonium perchlorate ion pairs⁵ III which are formed from *i*-ROAc and undissociated $HClO_4$ (rate constant k_i) and from

(1) This research was supported by the National Science Foundation and sponsored by the U. S. Army Research Office (Durham).

(2) Reported in part at the Third Caribbean Chemical Symposium, Caracas, Venezuela, Jan 4–9, 1965 [*Acta Cient. Venezolana*, **15**, 244 (1965)], and the Japanese-American Seminar in Physical-Organic Chemistry, Kyoto, Japan, April 6–10, 1965.

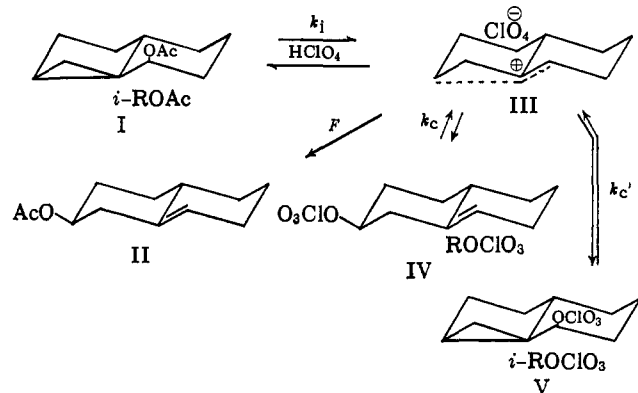
(3) (a) S. Winstein and E. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959); (b) G. H. Whitam and J. A. F. Wickramasinghe, *J. Chem. Soc.*, 1655 (1964); (c) J. H. Beynon, I. M. Heilbron, and F. S. Spring, *ibid.*, 907 (1936); (d) R. Snee and A. Ehret, unpublished work.

(4) We are indebted to Professor William Dauben, who first called our attention to the superiority of a zero-order plot for this isomerization.

(5) This representation is employed for simplicity, and no implications are intended as regards exact electronic structure^{3a,b} of R^+ and the variety of ion pairs⁶ involved.

(6) E.g., S. Winstein, P. E. Klinedinst, and G. C. Robinson, *J. Am. Chem. Soc.*, **83**, 885 (1961).

ROClO₃ (rate constant k_c) or *i*-ROClO₃ (rate constant k_c'). Of the carbonium perchlorate ion pairs III, some lead to *i*-ROAc, ROClO₃, and *i*-ROClO₃, and a fraction F gives rise irreversibly to ROAc. On this basis, the isomerization rate is given by eq 6. This may be transformed to (7), which reproduces the first-order dependence on (ΣHClO_4) and the zero-order dependence on (*i*-ROAc). On this basis, the k_1 of eq 2 is $F[(k_i/K_m^i) + k_c + (k_c'K_m^{ii}/K_m^i)]$.



$$K_m^i = \frac{(\text{ROClO}_3)}{(i\text{-ROAc})(\text{HClO}_4)} = ca. 2000 \quad (5)$$

$$\text{rate} = F[k_i(i\text{-ROAc})(\text{HClO}_4) + k_c(\text{ROClO}_3) + k_c'(i\text{-ROClO}_3)] \quad (6)$$

$$\text{rate} = F[(k_i/K_m^i) + k_c + (k_c'K_m^{ii}/K_m^i)](\Sigma\text{HClO}_4) \quad (7)$$



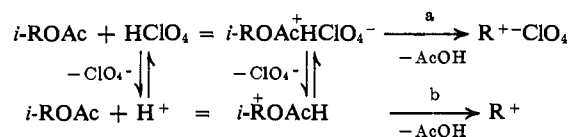
The substantial diversion of perchloric acid during isomerization of *i*-ROAc to ROAc can in fact be demonstrated by indicator studies. For example, using *p*-naphtholbenzein^{7a} as indicator, it is evident that addition of 0.0108 *M* *i*-ROAc to a 3.45×10^{-4} *M* HClO₄ solution reduces the available HClO₄ concentration initially to 1.70×10^{-5} *M*. Then, as *i*-ROAc isomerizes, the concentration of available HClO₄ returns to its original value. A series of such measurements leads to a value of *ca.* 2000 for the metathetical equilibrium constant⁸ K_m^i .

The present results are instructive in several ways. First of all, the observed substantial carbonium perchlorate ion-pair return is possible because acetic acid is a poorly dissociating solvent for ion pairs. In this solvent, the dissociation constant for HClO₄ is quite low⁷ and the dissociation constant for *i*-ROAcH⁺ClO₄⁻ is also low. This factor favors ionization route a to a carbonium perchlorate ion pair which can collapse to ROClO₃, rather than route b to dissociated carbonium ions, which are much less apt to yield ROClO₃.

(7) (a) I. M. Kolthoff and S. Bruckenstein, *J. Am. Chem. Soc.*, **78**, 1 (1956); (b) S. Bruckenstein and I. M. Kolthoff, *ibid.*, **78**, 2974 (1956); (c) T. L. Smith and J. H. Elliot, *ibid.*, **75**, 3566 (1953).

(8) The values of K_m^i drift somewhat with variations in the concentrations of *i*-ROAc and ΣHClO_4 , due at least in part to partial dissociation of the free HClO₄. A fuller account will be published elsewhere.

since this would require reassociation with a dissociated ClO₄⁻.



The present carbonium perchlorate ion-pair return is pertinent to the question of the general behavior⁶ of carbonium perchlorate ion pairs which are involved in the "special salt effect" of a perchlorate salt (*e.g.*, LiClO₄) in reducing ion-pair return during acetolysis of a substrate such as 3-anisyl-2-butyl bromobenzene-sulfonate. We previously inquired⁶ whether the components of the carbonium perchlorate ion pairs ever interact to the point of giving covalent perchlorate. However, as long as covalent perchlorate is extremely reactive relative to the solvolyzing substrate, none of the features of the kinetics of the special salt effect are affected by such carbonium perchlorate ion-pair return.⁶ In this context, the present work provides an actual example of carbonium perchlorate ion-pair return to covalent perchlorate.

The reason for substantial formation of ROClO₃ from *i*-ROAc, and not from ROAc, is the much greater free energy of *i*-ROAc relative to ROAc. Thus, during isomerization of *i*-ROAc to ROAc, the steady-state equilibrium (4), involving conversion of *i*-ROAc to ROClO₃, tends to be maintained. With the ratio of (ROClO₃) to (*i*-ROAc) controlled by eq 5, cholesteryl perchlorate is produced and temporarily maintained in amounts greatly exceeding the thermodynamic equilibrium proportions relative to cholesteryl acetate and perchloric acid. When isomerization of *i*-ROAc is complete, the concentration of cholesteryl acetate exceeds (*i*-ROAc) by a factor of *ca.* 10^{6.4}, since the K_{RX} for equilibrium 9 between cholesteryl and *i*-cholesteryl derivatives^{3a} is *ca.* 10^{6.4}. Now, the equilibrium proportions of ROClO₃ are controlled by equilibrium 8 between ROClO₃ and ROAc and HClO₄. The pertinent equilibrium constant K_m may be estimated to be of the order of 10⁻³, namely, (K_m^i/K_{RX}). Therefore, the equilibrium ratio of (ROClO₃) to (ROAc) is very small. For example, it is estimated to be *ca.* 10⁻⁵ when (HClO₄) is 0.01 *M*.

In the case of isolable materials such as ROTs or RCl, there are many illustrations of this same point where such products are obtained from HX and a high-energy isomeric acetate^{3d} or alcohol,^{3c} R'OAc or R'OH, but not the low-energy isomers, ROAc or ROH. A very interesting recent example concerns the isomeric dibenzocyclooctatrienyl (R'X) and dibenzocycloheptatrienylmethyl (RX) systems.⁹ Treatment with HOTs in AcOH leads to ROTs from R'OAc but not from ROAc.⁹

(9) E. Ciorănescu, A. Bucur, M. Elian, M. Banciu, M. Voicu, and C. D. Nenitzescu, *Tetrahedron Letters*, No. 51, 3835 (1964); *Rev. Roumaine Chim.*, **10**, 161 (1965).

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