of benzyl groups.[14] In situations in which phenyl is geometrically restricted from assuming an orientation favorable for phenonium ion formation, phenyl has a lower migratory aptitude than alkyl groups,[15] whereas phenyl migrates almost to the exclusion of alkyl migration when a phenonium ion can be achieved.[9] This is the result not of an inductive effect but of the hybridization of the bonding orbitals of the migrating carbon (sp^2, higher s character than alkyl, and more tightly bound), which must be used in migration of phenyl in cases in which phenonium ion formation is precluded. Since the bulk and hybridization of cyclopropane should decrease its migratory aptitude relative to methyl the nearly exclusive cyclopropyl migration observed in this system, **1**, indicates that the transition state for cyclopropyl migration is stabilized relative to the transition state for methyl and isopropyl migration, whereas in other systems migration of *sec*-alkyl is preferred over cyclopropyl.[2j,k]

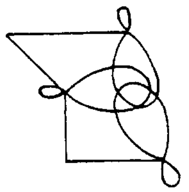
The relative stabilities of the tertiary carbonium ions formed by migration of cyclopropyl *vs.* methyl must be a minor factor in determining the migratory aptitudes as the preferential cyclopropyl migration observed leads to the less stable tertiary cation, as is also observed in the solvolysis of neophyl systems.[9] This suggests that stabilization of the transition state by delocalization of the positive charge developing at the quaternary neopentyl carbon is small compared to the stabilization gained by cyclopropyl or phenyl migration. These data support a mechanism for solvolysis in which ionization is assisted by cyclopropane participation which at the same time facilitates cyclopropane migration. On this basis partial rate factors for cyclopropyl (k_p^{Δ}), methyl ($k_p^{CH_3}$), and isopropyl ($k_p^{i\text{-Pr}}$) may be calculated from the rate and product data (Table II). Comparison of partial rate factors for cyclopropyl *vs.* isopropyl reveals enhancement of the cyclopropane-assisted solvolysis as a facter of 148.

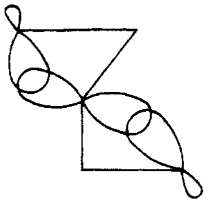
Table II. Partial Rate Factors for Migration of Alkyl Groups in Neopentyl Solvolyses at 75°

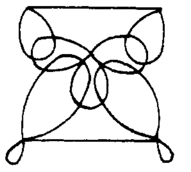
R	$k_{obsd} \times 10^7$ sec^{-1}	$k_p^{CH_3}$	k_p^{Δ}	$k_p^{i\text{-Pr}}$
CH_3[a]	3.44	1.15		
Cyclopropyl, **1**[b]	134	2.28	129	
Isopropyl, **2**	17.4	8.26		0.87

[a] Reference 8. [b] This work. [c] Calculated from data of Fritz,[13] 95% methyl migration, 5% isopropyl migration.

The type of orbital interaction between the cyclopropyl group and the reactive site in the transition state for ionization presents an intriguing quandary. There are no π-bonding centers in cyclopropane available for interaction as in phenyl or vinyl and stabilization of the transition state must result from delocalization of σ bonds of the ring which are high in p character. This might be pictured as cyclopropane ring–edge interaction, **10** (most probable for participation in 2-cyclopropylethyl), of the homocyclopropenyl type[16] and similar to cyclopropane protonation.[17] However no cyclopentyl products or other rearranged products were obtained as might be anticipated from this type of interaction. A second type of interaction similar to that proposed by Freeman and Balls,[18] **11**, also would not lead directly to the products observed. The simplest explanation, a simple Wagner–Meerwein rearrangement, does not account for the rate enhancement and preferential migration of cyclopropane. Modification of this transition state to include delocalization of both of the cyclopropane ring bonds, such as in **12**,[19] or rearrangement of an initially formed **10** or **11** to the tertiary carbonium ion **7** would account for the observed products and rates in the neopentyl case. Mechanistic economy, however, would be best served by a common transition state for the 2-cyclopropylethyl and cyclopropylneopentyl systems. The question of transition state and intermediate structures for the reactions of these simple cyclopropylethyl systems is being explored further.


10


11


12

---

[14] J. R. Owen and W. H. Saunders, Jr., *J. Amer. Chem. Soc.*, **88**, 5809 (1966).

[15] (a) J. W. Wilt, C. A. Schneider, J. P. Berliner, and N. F. Dobek, *Tetrahedron Lett.*, 4073 (1966); (b) W. E. Parham and L. J. Czuba, *J. Amer. Chem. Soc.*, **90**, 6876 (1968); (c) J. E. Nordlander and W. G. Deadman, private communication.

[16] S. Winstein, P. Bruck, P. Radlick, and R. Baker, *J. Amer. Chem. Soc.*, **86**, 1867 (1964).

[17] N. C. Deno, D. LaVietes, J. Mockus, and P. C. Scholl, *ibid.*, **90**, 6457 (1968), and references cited.

[18] P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967).

[19] A situation perhaps similar to that in tricyclopropylaluminum dimer: D. A. Sanders and J. P. Oliver, *J. Amer. Chem. Soc.*, **90**, 5910 (1968).

* To whom correspondence should be addressed.

Yorke E. Rhodes,* Toshio Takino
Department of Chemistry, New York University
New York, New York 10453

Received March 30, 1970

Identification of Pentacyanomonoaquochromate(III)[1]

Sir:

Schaap and coworkers[2–4] have described the preparation, isolation, and absorption spectra of a series of chromium(III) complexes of the form $Cr(CN)_n(H_2O)_{6-n}{}^{3-n}$. It was reported that the pentacyano complex ($n = 5$) undergoes rapid aquation to the tetracyano complex ($n = 4$) and is therefore difficult to isolate. In this communication we wish to report experimental evidence that the complex identified by Schaap and coworkers as the tetracyano complex is in fact the pentacyano complex.

We have recently investigated the kinetics of the chromium(II)-catalyzed aquation of hexacyanochromate(III) at 25°. The media for these studies were various combinations of NaCN, NaOH, and $NaClO_4$ (ionic strength = 1.0 *M*). When the concentrations of

---

[1] This work was performed under the auspices of the U. S. Atomic Energy Commission.

[2] R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967).

[3] R. Krishnamurthy, Ph.D. Thesis, Indiana University, 1966.

[4] W. B. Schaap, R. Kirshnamurthy, D. K. Wakefield, and W. F. Coleman in "Coordination Chemistry," S. Kirshner, Ed., Plenum Press, New York, N. Y., 1969, p 177.

both NaCN and NaOH are greater than 0.1 *M* and when the ratio [NaOH]/[NaCN] is less than 2, an equilibrium is established between the hexacyano complex and a species whose spectrum (at pH 5) is identical with the spectrum reported for the tetracyano species. Much to our surprise, however, the equilibrium between the two chromium(III) species as determined spectrophotometrically has a *first-order* dependence on the concentrations of both cyanide and hydroxide ions. This result is clearly contradictory to the stoichiometry implied by the conversion of the hexacyano to the supposed tetracyano complex. The first-order hydroxide ion dependence can be explained if the tetracyano complex were of the form $Cr(CN)_4(OH)(H_2O)^{2-}$. It is still paradoxical, however, that the cyanide ion dependence is first order and not second order. The stoichiometry of the reaction with respect to cyanide was determined by using a high concentration (0.2 *M*) of the hexacyano complex and measuring the change in the cyanide concentration resulting from the aquation:[5] a change of one cyanide per molecule of hexacyano complex aquated was found. On the basis of these experiments we were forced to consider the possibility that the aquation product might be $Cr(CN)_5(OH)^{3-}$.

To verify this possibility the supposed tetracyano complex was prepared according to the published procedures[3,4] and analyzed for bound cyanide. The analytical technique requires cleavage of the cyanides followed by a cyanide determination. After determining the concentration of the complex spectrophotometrically, an aliquot (3–5 ml) was acidified with $HClO_4$ to $\approx$0.25 *M* in a sealed flask, causing aquation primarily to the tricyanotriaquochromate(III) complex and to some extent to more highly aquated species. After 15 min the solution was made basic with NaOH (to $\approx$0.2 *M*) causing spontaneous aquation to the hexaquochromate(III) complex. In titrating the free cyanide with a solution of $AgNO_3$ (0.0233 *N*), we determined the end point by following the pCN with the cyanide electrode (see ref 5). The results of the titrations are shown in Table I and clearly indicate that five cyanides were liberated per molecule of the complex (in contradiction to the reported value of four[3,4]).

Table I. Titration of Cleaved Cyanides

[Complex][a]	Vol of complex, ml	Vol of $AgNO_3$, ml[b]	$[CN^-]/[Cr]$
0.0160 (a)	3.00	10.20	4.95
0.0160 (a)	3.00	10.25	4.98
0.00287 (b)	5.00	3.12	5.07
0.00552 (c)	5.00	5.87	4.96
0.00552 (c)	5.00	5.90	4.98
0.00320 (d)	5.00	3.37	4.91
			Av = 4.98 ± 0.05

[a] a, b, c, and d in parentheses indicate separately prepared samples. [b] 0.0233 *N*.

The free cyanide introduced during the preparation of the complex was removed by argon purging at pH 5. Measurement of the pCN prior to aquation indicated that there was less than 0.2 free cyanide per molecule of complex.

In a similar experiment the tricyano complex was prepared and analyzed for cyanide: three cyanides per molecule of complex were found.

Using the basic aquation technique described by Schaap, *et al.*,[3,4] which requires heating to effect aquation to a chromic oxide precipitate, we found that prolonged heating causes a loss of free cyanide. Prolonged heating of alkaline NaCN solution also diminishes the titer of free cyanide. This probably explains the low value obtained by Schaap, *et al.*[3,4]

A solution containing what we now believe to be the pentacyano complex was adjusted to pH 4 and titrated with NaOH. The pH was followed and showed a single break corresponding to 1 equiv of base/mol of complex. The p*K* for this acid–base equilibrium is 9.0. Furthermore, the complex exhibits only two distinct spectra in the pH range 4–14. One spectrum remains constant in the pH region 4–7 (acid-catalyzed aquation commences at pH <4) and the second in the pH region 11–14 (1 *M* NaOH). Thus if a second acid–base reaction exists (as it should for the tetracyano complex) we saw no indications of it in this pH range.[6]

Some corroborative evidence for a stable pentacyano complex is indicated by the work of Chiang and Adamson.[7] They studied the photoaquation of the hexacyano complex to a product assumed to be the tetracyano complex on the basis of the reported spectra. Although their experimental conditions were not rigorously controlled a comparison of the number of cyanides released per molecule of the hexacyano complex during photolysis (Figure 1 of ref 7) with the fraction of hexacyano complex converted to product (Figure 3 of ref 7) suggests that one cyanide is released per molecule converted. This is difficult to explain unless the product is the pentacyano complex.

On the basis of these data we are confident that the species which has heretofore been identified as the tetracyano complex is in fact the pentacyano[8] complex $Cr(CN)_5(H_2O)^{2-}$. The analysis indicates that it contains five cyanides; a pH titration indicates only one acidic proton; and the chromium(II)-catalyzed equilibrium between the hexacyano and pentacyano complexes has a first-order dependence on cyanide as described by the following equation

$$K_{eq} = 0.8 = \frac{[Cr(CN)_5(OH)^{3-}][CN^-]}{[Cr(CN)_6^{3-}][OH^-]}$$

Since the analysis of the tricyano complex confirms that it contains three cyanides per molecule, the tetracyano complex appears to be the elusive form.

Acknowledgment. The authors thank Dr. Norman Sutin for his continued interest and valuable comments during the course of this work. Mr. S. J. Tassinari is thanked for his assistance with several aspects of the

---

[5] The pCN of the solutions before and after conversion was measured using the Orion cyanide electrode (Model 94-06, Orion Research Inc., Cambridge, Mass.). The chromium cyanide complexes interfere with a silver nitrate titration.

[6] Reported p*K* values for the three acid–base equilibria of the tricyano complex (ref 4), 6.8, 9, and 10.5, suggest that the two p*K* values for the tetracyano complex should be separated by about 2 p*K* units. Thus if one p*K* is 9 the other ought to be about 7 or 11, and should have been observed.

[7] A. Chiang and A. W. Adamson, *J. Phys. Chem.*, 72, 3827 (1968).

[8] Schaap, *et al.*,[2–4] have presented the spectrum of a complex which they designated as the pentacyanomonoaquochromate(III) complex. The extremely low yield in the preparation of their complex and the absence of any analysis for the $[CN^-]/[Cr]$ ratio make this identification tenuous. We did not attempt to prepare or analyze their complex.

instrumentation and calculations associated with our work.

(9) (a) On leave from the "Rudjer Bošković" Institute, Zagreb, Yugoslavia; (b) address correspondence to this author.

Ljubomir Jeftić,[9a] **Stephen Feldberg**[9b]
Department of Applied Science
Brookhaven National Laboratory, Upton, New York 11973

Received May 22, 1970

Cation Radicals. I. Chlorination of Carboxylic Acids *via* Oxygen Cation Radicals. The McLafferty Rearrangement in Solution

Sir:

The Hofmann–Löffler reaction is the selective internal chlorination of amines at C-4 *via* a nitrogen cation radical in a six-membered cyclic transition.[1–3] Alkyl hypochlorites, both primary[4] and tertiary,[5–8] also selectively chlorinate C-4. The Barton[9] and Yang[10] reactions also involve selective abstraction of H from C-4. Even in mass spectra, oxygen cation radicals abstract H internally and selectively at C-4 (McLafferty rearrangement).[11] All of these reactions are free-radical processes. By their precedent, selective H abstraction at C-4 is diagnostic for such internal, free-radical H abstractions *via* six-membered cyclic transition states.

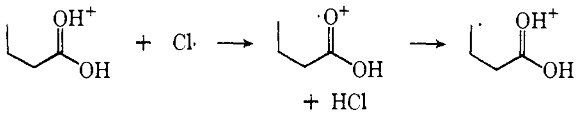
We have now observed selective chlorination at C-4 in butyric, hexanoic, and octanoic acids by conducting the chlorination of these acids in 90% H_2SO_4 (Table I).

Table I. Yields of Monochloro Acids Based on RCOOH Consumed[a]

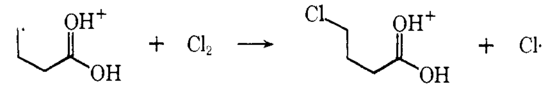
RCOOH[a]	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl
	Cl_2, 90% H_2SO_4, 25°						
Octanoic acid	5	8	31	10	2	3	41
Octanoic acid[b]	3	6	27	8	2	3	51
Hexanoic acid	4	7	40	7	42		
Butyric acid	0	21	79				
	Cl_2, CCl_4, 25°						
Octanoic acid	1.5	9	15	15	19	24	17
Hexanoic acid	4	13	28	37	18		
Butyric acid	5	53	42				
	Cl_2, C_6H_6, 25°						
Octanoic acid	0	3	14	24	30	26	3
	tert-BuOCl, CCl_4, 25°						
Octanoic acid	6	7	14	17	22	28	6

[a] Twofold excess of RCOOH over Cl_2. [b] Reaction conducted at 60°.

The reasons for interpreting this selectivity as due to an oxygen cation radical process, eq 1, are identical with those used in establishing the nitrogen cation radical mechanism for the Hofmann–Löffler reaction.[1–3] These are: (1) the reaction abstracts H at C-4, (2) the reaction fails with chains shorter than four carbons (in our case, propionic and acetic acids reacted very slowly), (3) the selectivity was not affected by concentration of reactant, (4) the reaction is photochemical with very high quantum yields (in our case, 0.1 mol of RCOOH reacted completely in 1 hr with sunlamp irradiation), and (5) the selectivity is found only in highly acidic systems.



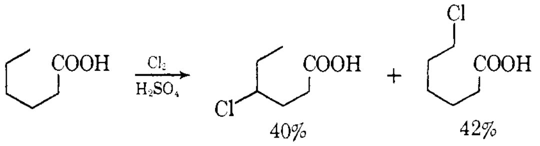
(1a)



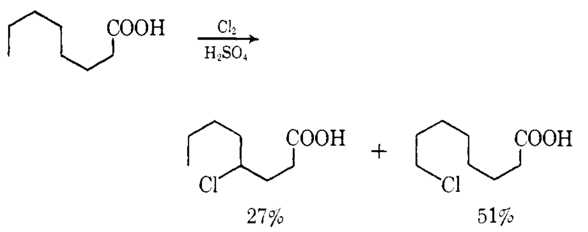
(1b)

Table I includes data on chlorination of butyric, hexanoic, and octanoic acids in CCl_4 to show the near randomness of the chlorinations in CCl_4 and the dramatic contrast with chlorinations conducted in 90% H_2SO_4. Chlorination of octanoic acid by the more selective reagents (*tert*-BuOCl and $C_6H_6Cl\cdot$) are also included in Table I and these are also nearly random except for the marked reduction in the chlorination of the primary hydrogens (terminal methyl) and the usual avoidance of α chlorination at C-2.

In addition to the selective chlorination on C-4, hexanoic acid gives a comparable amount of chlorination on C-6 (eq 2) and octanoic acid gives a comparable amount of chlorination on C-8 (eq 3). Experiments are in progress to see if these patterns are followed in the Hofmann–Löffler, alkyl hypochlorite decomposition, and the Barton and Yang reactions.



(2)



(3)

Regardless of the mechanism, the selective chlorinations illustrated in eq 2 and 3 are most novel and represent the highest yields of ω chlorination that have been achieved.

Several amino and diamino carboxylic acids have been chlorinated in good yield in 90% sulfuric acid.[12] The alkyl chains were generally too short to detect the effects shown in Table I and the presence of one or two NH_3^+ substituents complicated the problem.

---

(1) M. E. Wolff, *Chem. Rev.*, 62, 55 (1962).

(2) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 280 ff.

(3) E. J. Corey and W. R. Hertler, *J. Amer. Chem. Soc.*, **82**, 1957 (1960).

(4) E. L. Jenner, *J. Org. Chem.*, 27, 1031 (1962).

(5) F. D. Greene, M. L. Savitz, H. H. Lau, D. Osterholtz, and W. M. Smith, *J. Amer. Chem. Soc.*, **83**, 2196 (1961).

(6) C. Walling and A. Padwa, *ibid.*, **83**, 2207 (1961).

(7) M. Akhtar and D. H. R. Barton, *ibid.*, **83**, 2213 (1961).

(8) J. S. Mill and V. Petrov, *Chem. Ind. (London)*, 946 (1961).

(9) D. H. R. Barton, J. M. Beaton, L. E. Geller, and M. M. Pechet, *J. Amer. Chem. Soc.*, **82**, 2640 (1960).

(10) N. C. Yang and D. H. Yang, *ibid.*, **80**, 2913 (1958).

(11) For a recent review, see H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, Calif., 1967, Chapter 3.

(12) J. Kollonitsch, A. Rosegay, and G. Doldowias, *J. Amer. Chem. Soc.*, **86**, 1857 (1964).