

Figure 1. Schematic representation of infrared absorptions of (A) anhydrous hydroxytropenium iodide, (B) hydroxytropenium iodide monohydrate, (C) anhydrous hydroxytropenium bromide, (D) partially hydrated hydroxytropenium bromide, and (E) previously reported "hydroxytropenium bromide."⁸

band in this region at 2390 and 2410 cm^{-1} , respectively; (2) in deuterioxytropenium bromide (prepared from tropone and dry deuterium bromide) the 2390- cm^{-1} band shifts to 1860 cm^{-1} for a $\nu_{\text{H}}/\nu_{\text{D}}$ ratio of 1.28⁹; and (3) methoxytropenium fluoroborate^{3,11} shows no absorption in this region.¹²

Vol'pin, *et al.*,⁸ report that hydroxytropenium bromide shows a strong band at 3125 cm^{-1} and medium broad bands at 2387 and 1876 cm^{-1} ; they assign the 3125- cm^{-1} band to O-H stretch in the cation and the other two bands to O-H-Br hydrogen bonding. We have prepared anhydrous hydroxytropenium bromide as light yellow plates (*Anal.* Calcd. for $\text{C}_7\text{H}_7\text{BrO}$: $\text{C}_7\text{H}_6\text{OH}^+$, 57.27; Br^- , 42.72. Found: $\text{C}_7\text{H}_6\text{OH}^+$, 56.9; Br^- , 42.91) and find that it shows only the broad band at 2390 cm^{-1} . When the yellow bromide is exposed to moist air it turns white, and it will deliquesce with excess moisture to form yellow solutions. Evaporation of such solutions leaves white needles which show a strong absorption at 3100 cm^{-1} , a medium broad band at 1870 cm^{-1} , and a weak band at 2390 cm^{-1} . We believe this latter band to be due to unhydrated bromide present, and the other two bands to be hydrate absorptions.

The data presented herein clearly indicate that the O-H stretching frequency of the hydroxytropenium cation is a broad band in the 2300-2700- cm^{-1} region. The position of this band is anion dependent, which suggests O-H-X hydrogen bonding. This band under-

(9) This ratio, normally 1.35 for the shift of an O-H frequency on deuteration, is often slightly reduced in the solid state.¹⁰

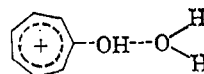
(10) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif., 1960, p. 111, and references therein.

(11) H. J. Dauben, Jr., and K. M. Harmon, unpublished work in Ph.D. Thesis of K. M. H., University of Washington, 1958.

(12) All of these salts show C-H absorptions in the vicinity of 3000 cm^{-1} ; these bands are small compared to the O-H bands under discussion and are easily distinguished from them.

goes a large shift to lower energies with hydrate formation indicative of strong hydrogen-bond formation,¹⁰ and the O-H stretching band of the water of hydration appears as an intense absorption in the 3100-3300- cm^{-1} region with slight anion dependence. Vol'pin, *et al.*,⁸ were dealing with a hydrate; this fact is supported by the published⁸ infrared spectrum of their tropone starting material. This tropone was clearly wet, as it contains a strong band at 3400 cm^{-1} which is found in wet tropone, but not in material which has been rigorously dried.¹³

The above spectral and thermochemical data suggest that the water in hydrates of hydroxytropenium ion is strongly hydrogen bonded to the -OH on the cationic ring and that secondary hydrogen bonding of the hydrogens of water to halide ion is also probably present. Such hydrogen bonding could account for the



change in color of the iodide from red to yellow on hydration, since the net effect would be to increase the electron density of the ring and make it a poorer acceptor for the charge-transfer⁴ transition which causes the color of such salts.

The observed enthalpy change represents the difference between the enthalpy of hydrogen-bond formation and the differential lattice enthalpy,¹⁴ *i.e.*, the change in enthalpy of the crystal lattice on hydrate formation. Since for the dissociation process $\Delta H^\circ_{(1)}$ is almost surely negative, 14 kcal./mole would seem a reasonable lower limit for the strength of the hydrogen bond in hydroxytropenium iodide monohydrate.

(13) Y. Ikegami, *Bull. Chem. Soc. Japan*, **35**, 967 (1962), gives the infrared spectrum of dried tropone. The last water is remarkably difficult to remove.

(14) K. M. Harmon, S. D. Alderman, K. E. Benker, D. J. Diestler, and P. A. Gebauer, *J. Am. Chem. Soc.*, **87**, 1700 (1965).

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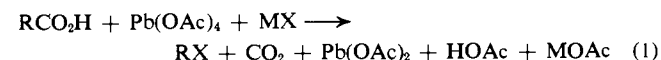
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A New Method for Halodecarboxylation of Acids Using Lead(IV) Acetate

Sir:

Synthetically, carboxylic acids are decarboxylated with halogens to alkyl halides through the agency of the dry silver salt,¹ or in modified procedures directly with mercuric oxide or lead acetate.² We wish to report a convenient method for the decarboxylation of acids with lead tetraacetate and *ionic halide* (particularly chloride) salts (MX).

The stoichiometry of the reaction as written in eq. 1 is suggested.



(1) (a) R. G. Johnson and R. K. Ingham, *Chem. Rev.*, **56**, 219 (1956); (b) C. V. Wilson, *Org. Reactions*, **9**, 332 (1957).

(2) (a) S. J. Cristol and W. Firth, Jr., *J. Org. Chem.*, **26**, 280 (1961); **27**, 2711 (1962); (b) J. A. Davis, *et al.*, *ibid.*, **30**, 415 (1965); (c) D. H. R. Barton and E. P. Serebryakov, *Proc. Chem. Soc.*, 309 (1962); (d) G. B. Bachman and J. W. Wittman, *J. Org. Chem.*, **28**, 65 (1963).

Table I. Formation of Alkyl Chlorides from Lead(IV) Acetate and Lithium Chloride^a

Acid (mequiv.)	LiCl, mequiv.	Methyl chloride, % ^b	Alkyl chloride (% ^b)
None	10	55 ^c	
Isobutyric (10)	6.2	0	Isopropyl chloride (98) ^d
Valeric (20)	4.6	4	<i>n</i> -Butyl chloride (92) ^e
Valeric (9.2)	4.6	6	<i>n</i> -Butyl chloride (87) ^e
Valeric (4.9)	4.6	..	<i>n</i> -Butyl chloride (66) ^e
Isovaleric (20)	4.7	1	Isobutyl chloride (99) ^e
α -Methylbutyric (20)	11	0	<i>sec</i> -Butyl chloride (96) ^d
α -Methylbutyric (4.6)	4.7	4	<i>sec</i> -Butyl chloride (87) ^d
Pivalic (9.5)	6.3	0	<i>t</i> -Butyl chloride (72) ^{d,f}
α,α -Dimethylbutyric (18)	6.6	0	<i>t</i> -Amyl chloride (91) ^{d,g}
β,β -Dimethylbutyric (8.6)	6.2	7	Neopentyl chloride (92) ^e
Allylacetic (10)	6.9	..	4-Chlorobutene-1 (2) ^h
Cyclobutanecarboxylic (9.2)	6.2	1	Cyclobutyl chloride (98)
Cyclohexanecarboxylic (15)	6.4	0	Cyclohexyl chloride (100) ^d
Benzoic (13)	6.7	58	Chlorobenzene (8)

^a In benzene solutions (10 ml.) containing 4.5 mequiv. of lead acetate at 81°. Analysis by gas chromatography. ^b All yields based on lead(IV) acetate. ^c In addition to chlorobenzene (3%) and chlorine. ^d No chlorobenzene. ^e Traces of chlorobenzene. ^f 9% isobutylene. ^g 4% 2-methylbutene-1 and 4% 2-methylbutene-2. ^h Other products unidentified.

The reaction is conducted by adding 1 equiv. of halide to a solution of the acid and lead(IV) acetate in benzene. The mixture is swept with nitrogen and heated to 80° with stirring. With LiCl and CaCl₂, though initially heterogeneous, the reaction is complete within a few minutes. The very insoluble KCl and NaCl require longer heating. Acetonitrile and hexane-benzene mixtures can also be employed as solvents, and potentially a variety of others are available. No particular precaution is exercised to remove adventitious water. The completion of the reaction is characterized by a change in color from pale yellow^{3a} to water white, and in the presence of excess acid the mixture employing LiCl becomes homogeneous. Air strongly inhibits the reaction and flushing with inert gas is critical for facile reaction.

Lead(IV) acetate itself under these conditions is readily decarboxylated to methyl chloride (40–60%), methylene chloride (trace), and chlorine. Decarboxylation is most rapid with tertiary or secondary acids, and formation of methyl chloride is unimportant. Primary acids also afford alkyl chlorides in high yields, and methyl chloride accompanies the primary chlorides. Methyl chloride can be reduced (from 10 to 1%) by increasing the ratio of acid to lead(IV) acetate (from 1 to 8). For maximum utilization of lead(IV) acetate, excess acid (which can be recycled) is desirable. Moreover, if adulteration by methyl chloride is not a problem, even primary acids can be converted to alkyl chlorides in excellent yields by using excess lead(IV) acetate. Representative (not optimum) examples are listed in Table I.

Optimum conditions require 1 equiv. of LiCl per mole of lead(IV) acetate. Yields of product fall off with increasing LiCl. If 4 equiv. is used the yield of alkyl chloride from valeric acid is nil and copious amounts of chlorine are released. If less than 1 equiv. of LiCl is employed, the reaction proceeds smoothly until the chloride is consumed and stops.^{3b} The utilization of chloride under these conditions to effect chlorodecarboxylation of valeric acid is >95%. The stoichiometric ratio of chloride to lead(IV) acetate is not a critical problem with the much less soluble

NaCl and KCl. Tetramethylammonium chloride which represents the most soluble salt studied gave the poorest yields of alkyl chloride, and the formation of excessive amounts of chlorine was evident.

Decarboxylation to alkyl bromides and iodides can also be effected with bromide and iodide salts. Isobutyric acid and LiBr afford isobutyl bromide in 50–60% yields. The formation of bromine is apparent, and during the course of the reaction it disappears (probably by bromination of the acid). Large amounts of iodine are produced from lead(IV) acetate and KI, and the yields of isopropyl iodide are low. The latter is not surprising in view of the iodometric procedure for the analysis of lead(IV) acetate.⁴

t-Butylacetic acid yields neopentyl chloride, and cyclobutanecarboxylic acid affords cyclobutyl chloride in high yields. Products of rearrangement characteristic of carbonium ions are not evident. Tertiary acids such as pivalic and α,α -dimethylbutyric acid form the corresponding chlorides in good yields, but small amounts of isobutylene and 2-methylbutenes, respectively, are also formed, probably by subsequent dehydrohalogenation. Benzoic acid gives poor yields of chlorobenzene accompanied by major amounts of methyl chloride. Unsaturated compounds represented by allylacetic acid undergo additional reactions since only traces of 4-chlorobutene are detectable.

Butane is a minor product from valeric acid and LiCl, and butene-1 is a major product (10–20%) with CuCl₂ (together with butyl chloride), both of which are symptomatic of free radicals.⁵ The inhibition by oxygen and the lack of skeletal rearrangement of neopentyl and cyclobutyl moieties are additional evidence for free-radical intermediates. We propose that the decarboxylation of lead(IV) carboxylates by halide is a free-radical chain process which occurs by a sequence of reactions analogous to that described earlier⁶ for oxidative decarboxylation in the absence of halide.

Except for the addition of halide salt and shorter time for reaction, the halodecarboxylation is conducted under essentially the same conditions as those for oxida-

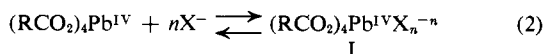
(4) R. C. Hockett and W. S. McClenahan, *J. Am. Chem. Soc.*, **61**, 1667 (1939).

(3) (a) Reactions with KCl and NaCl remain colorless throughout. (b) If heated longer, presumably the much slower oxidative decarboxylation⁶ will occur until Pb(IV) is completely reduced.

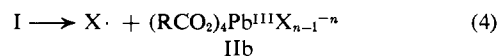
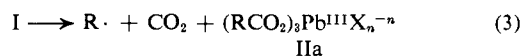
(5) H. E. De la Mare, J. Kochi, and F. F. Rust, *ibid.*, **85**, 1437 (1963); J. K. Kochi, *ibid.*, **85**, 1958 (1963).

(6) J. K. Kochi, *ibid.*, **87**, 1811 (1965).

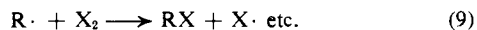
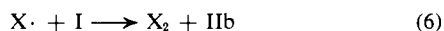
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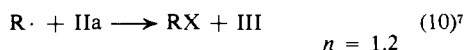
Initiation:



Propagation:



Termination:



tive decarboxylation.⁶ The pertinent difference between the mechanism for oxidative decarboxylation and halodecarboxylation is attributable primarily to the complexing of the propagation steps.⁸ Ligand transfer oxidation of alkyl radicals by species such as I and II has been delineated earlier.⁹ Lead(IV) carboxylates are reasonably stable, and the rapid decomposition in the presence of halide is attributed to the lability of anionic complexes such as I (eq. 3, 4), similar to the catalysis by acetate¹⁰ and bases¹¹ in oxidative decarboxylations.⁶ We consider halogen to be a side product and not an important intermediate^{2c} in the halodecarboxylation reaction. Thus, cyclohexyl chloride formed quantitatively from cyclohexanecarboxylic acid in benzene is an unimportant product (~2%) when the same reaction is carried out in the presence of added chlorine (chlorobenzene is the preponderant product). Halogens probably arise¹² by sequence 4, 6, and 8, and disappear by radical chain halogenation of the substrates; they assume greater importance in the order $\text{Cl} < \text{Br} < \text{I}$.

(7) Alternative modes of decomposition of IIa and IIb are also possible. The principal reactions in the propagation sequence are (5) and (7).

(8) We do not favor acyl hypohalites by reactions such as 11, 12, or 13 as prime intermediates since they readily form halogen in the



presence of halide [J. Kochi, B. M. Graybill, and M. Kurz, *J. Am. Chem. Soc.*, **86**, 5257 (1964); J. Kochi and R. V. Subramanian, *ibid.*, **87**, 1508 (1965)]. Moreover, the ease of decarboxylation, tertiary > secondary > primary, is contrary to the order found in the Hunsdiecker reaction,^{1,2} but it is the same as that in oxidative decarboxylation.⁶

(9) C. H. Bamford, A. Jenkins, and R. Johnston, *Proc. Roy. Soc. (London)*, **A239**, 214 (1957); J. K. Kochi and D. M. Mog, *J. Am. Chem. Soc.*, **87**, 522 (1965).

(10) D. Benson, L. Sutcliffe, and J. Walkley, *ibid.*, **81**, 4488 (1959).

(11) C. A. Grob and A. Weiss, *Helv. Chim. Acta*, **43**, 1340 (1960).

(12) Formation of halogen is facilitated by soluble salts of halides. An alternative route is $\text{I} + \text{X}^- \rightarrow \text{X}_2 + (\text{RCO}_2)_3\text{Pb}^{\text{III}} + 2\text{RCO}_2^-$ or similar nucleophilic displacements (e.g., eq. 11).^{8b}

(13) The author wishes to thank the National Science Foundation for generous support of this work.

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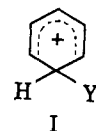
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A Correction to the Hückel Localization Energy Approximation of Aromatic Substitution Rates

Sir:

A familiar approach to the problem of predicting relative aromatic substitution rates is to treat the transition state in terms of a structure such as I.



Streitwieser¹ has defined a reaction hydrocarbon constant σ_r based on the linear free-energy relationship

$$\log k_r/k\alpha(\text{C}_{10}\text{H}_8) = \sigma_r\rho^* \quad (1)$$

where $\rho^* = 1$ for the protonation equilibria of aromatic hydrocarbons in hydrogen fluoride. Other electrophilic substitution rates are used to evaluate σ_r for hydrocarbons for which the protonation equilibrium constant is not available. These σ_r values give fair to good correlations with simple Hückel calculations of the localization energies L^+ and L^0 . The localization energies are defined as the difference in π -energy between the aromatic hydrocarbon and the carbonium ion I.

The equilibrium constants for protonation of aromatic hydrocarbons in hydrogen fluoride are found to give a good correlation with Hückel localization energies including overlap, except for pyrene and perylene,² which deviate considerably from the regression line.

A large source of error in either a simple Hückel calculation, or ω -type calculation,³ arises from the difference in charge of the electron core of the reactant and transition state. As one-electron localization energies, the error in neglecting this "core" difference in such calculations is not as likely to cancel for electrophilic and nucleophilic aromatic substitution as in a case such as free-radical addition wherein reactants and transition state have the same charge. If self-consistent field localization energies, which should remove this "core" error, are used, an excellent linear correlation is obtained⁴ with the protonation constants in which pyrene and perylene no longer deviate from the line.

The following thermodynamic arguments supply a correction by which the Hückel localization energies may be easily improved without the work of carrying out a self-consistent field calculation.

For a given reaction series with the same electrophile in the same solvent E_a and E_s will be constant. The variation of E_h with substrate hydrocarbon is more uncertain but will be considered as nearly constant in this approximation. If then ΔE is taken as either equal to or proportional to the activation energy the log of the substitution rate should be a linear function of $Ip + L\cdot$.

(1) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 307-350.

(2) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp. 97-99.

(3) A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960).

(4) A. A. V. Stuart and J. A. Kruijzinga, Quantum Chemistry Symposium, Paris, Sept. 1957, p. 229.