effects are generally absent. The H_- function is thus a good deal more comprehensive than its H_0 counterpart.[35,36])

We consider that the pK_a values given in Table IV are a better approximation to thermodynamic pK_a's than the H_0 (half-protonation) values also included in this table. This would not necessarily invalidate correlations of other parameters defining properties of such molecules with H_0 (half-protonation) values. Hence, previous correlations in the literature of these values with σ^+ for substituted benzaldehydes,[5] acetophenones,[2] and benzoic acids[3] are quite valid, provided the values of m are the same for all the bases considered, the m value in such cases being incorporated in ρ. In the same way, the correlation of σ with pK_a reported for substituted benzamides[37] is appropriate, even though later work showed these compounds to be following H_A; however, the ρ value is 0.78 (1.30 × 0.6) rather than 1.30. In this connection, however, we note from Table IV that the m value for benzaldehyde is substantially different from that for *p*-methoxybenzaldehyde; perhaps it is significant that the methoxy substituent gives a poor correlation in σ^+ plots.[2,3,5] In fact, experimental work on the various acidity functions has demonstrated that it is the functional group being protonated which decides the acidity function being followed, rather than the substituent adjacent to that particular function, usually attached *via* an aromatic nucleus. (Anomolous effects of the nitro group on solvation and hence acidity–activity coefficient variation behavior, the Hammett–Chapman effect, have been evaluated.[38,39] However, it appears that such effects will largely cancel since one is considering in any acidity function terms such as (log f_{BH^+} − log f_B). In any case, recent work suggests that the effect is small.[40])

Our results demonstrate that these compounds do not follow the H_A scale, and protonate more steeply than amide bases, with increasing acidity. Any acidity function H_x is defined by the equation $H_x = \log f_{BH^+}/a_{H^+}f_B$, and for a given set of bases to follow the same acidity function, the ratio f_{BH^+}/f_B must be the same at the same acidity. Attempts to define the change of f_{BH^+}/f_B with acidity in terms of specific hydration numbers[12] has been criticized,[41] but it appears reasonable to explain qualitatively the difference between the various scales (and therefore between m values) in terms of differing degrees of solvation, at a given acidity, of both the cationic and free base species of the various basic types.

The correlation of pK_a values with other physical properties of these molecules has already been indicated. An important aspect of these pK_a values would appear to be in the field of aromatic electrophilic substitution, where an accurate determination of rates of nuclear hydrogen exchange or nitration in such compounds, using solutions in concentrated sulfuric acid, requires a knowledge of accurate pK_a values and acidity function behavior. Such a program is in hand elsewhere;[42] it appears to represent an extension of the principles elucidated by Ridd, Schofield, and Katritzky, and coworkers, for the study of such reactions in heteroaromatic species.[43]

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Carbonium Ions. XXI. Protonated Cyclopropane[1]

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Abstract: Further evidence is obtained for the existence of protonated cyclopropane as a chemical species. Its stability is estimated to be intermediate between the isomeric 1-propyl and 2-propyl cations. In reactivity, it is unselective in alkylating toluene indicating high reactivity as an alkylating agent. In contrast, it is unable to abstract hydride from branched alkanes.

Protonated cyclopropane, c-$C_3H_7^+$, was proposed as an intermediate to explain the formation of cyclopropane from the nitrous acid deamination of propylamine.[3] Since then, a variety of observations have found explanations in terms of protonated cyclopropane intermediates.[4-10]

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Table I. Distribution of Deuterium in *n*-Propyl Derivatives Arising from Addition of Deuterated Reagents to Cyclopropane[a]

Reagent	Product	Total D introduced	% D (or T) at C-1	% D (or T) at C-2	% D (or T) at C-3
57% D_2SO_4[b]	1-PrOD and 1-$PrOSO_3D$	1.00	38	17	46
60% *t*-H_2SO_4[c]	1-PrOH and 1-$PrOSO_3H$		37	26	37
79% *t*-H_2SO_4[c]	1-$PrOSO_3H$		38	26	36
83% D_2SO_4	1-$PrOSO_3D$	(1.5)[d]	~28	~28	~44
92% D_2SO_4	1-$PrOSO_3D$	1.5[e]	~28	~28	~44
92% D_2SO_4	1-$PrOSO_3D$	1.0[e,f]	~28	~28	~44
99% D_2SO_4	1-$PrOSO_3D$	2.0[e]	30	29	42
20% CH_3COOD–80% D_2SO_4	1-Propyl acetate	1.6[g]	28	34	38
CF_3COOD	1-Propyl trifluoroacetate	1.0[h]	28	28	43
t-HCl–$ZnCl_2$[c]	1-Chloropropane		38	19	43
DCl (15% $FeCl_3$)[i]	1-Chloropropane	1.0[h]	35	26	39
D^+ (*c*-C_6D_6)	60% *n*-propylbenzene 40% isopropylbenzene	1.0[j]	28	28	43

[a] At 25° unless otherwise noted. [b] Reference 5. [c] Reference 8. [d] Assumed. [e] Determined by weighing the cyclopropane introduced and comparing nmr band areas to that of a standard, $(CH_3)_4NCl$. The conversion of cyclopropane to 1-propyl hydrogen sulfate was 100%. [f] The surface was flushed with N_2 to remove deuterated cyclopropanes. [g] The methyl group of the acetate served as an internal standard. [h] The product was isolated by distillation and the nmr band areas compared with those of a standard. [i] Reaction was conducted at the boiling point of cyclopropane, −34°. [j] Required by the stoichiometry since no hydrogen appeared on the phenyl ring.

The critical experiment in establishing the existence of *c*-$C_3H_7^+$ was that of Baird and Aboderin.[5] They introduced cyclopropane into 57% D_2SO_4, hydrolyzed the products, extracted and isolated the 1-propanol by gas chromatography (gc), formed the *p*-toluate ester, and determined the deuterium distribution by nmr. The remarkable result was that the deuterium was 38% on C-1, 17% on C-2, and 46% on C-3. This scrambling was interpreted as arising through addition of D^+ to cyclopropane to form I and II. These isomerize to the other two isomeric forms of I and the one other isomeric form of II. The equilibrating

I II

system is trapped, by HSO_4^- or H_2O, before equilibration was complete, leading to a nonstatistical distribution of deuterium.

It was thought that the Baird and Aboderin experiment should be confirmed and elaborated by determining the deuterium distribution in a more direct way. Further, conditions of longer life for *c*-$C_3H_7^+$ should be sought in which equilibration would be more complete. It was also desired to estimate the stability of *c*-$C_3H_7^+$ relative to other carbonium ions and to assess something of its chemistry and reactivity.

Further Evidence for Protonated Cyclopropane. Five reagents have been added to cyclopropane under acidic conditions. The data are summarized in Table I along with data from ref 5 and 8. In our work, the deuterium distributions were calculated from the total deuterium introduced coupled with relative areas of the nmr bands of the propyl group. The nmr spectra were measured directly on the reaction mixtures except for the addition of DCl and deuterated benzene (*c*-C_6D_6) in which cases the product was first washed with water.

In all but the *c*-C_6D_6 experiment, the product was entirely the *n*-propyl product with no trace of isopropyl. This predominance of *n*-propyl product has been noted before in H_2SO_4 additions,[5,11] acetic acid addition,[11] and alkylations of alkylbenzenes.[12] Figure 1 is an nmr spectrum of the chloropropane from HCl plus cyclopropane. It is typical and illustrates the exclusive formation of *n*-propyl product. Figure 2 is the companion spectrum for DCl plus cyclopropane. The distribution of deuterium on all three carbons is evident from the splitting pattern alone.

The Baird–Aboderin interpretation,[5] intermediate isomerizing *c*-$C_3H_6D^+$ species, is accepted for the results in Table I. A particularly important result is that the deuterium scrambling approaches statistical as the D_2SO_4 concentration increases and, at 98% D_2SO_4, the distribution is within experimental error of the statistical 28.5:28.5:5:43 (Table I). This experimentally demonstrates that when the lifetime of *c*-$C_3H_6D^+$ is long enough to achieve complete equilibrium between isomeric forms, statistical distribution results and kinetic and equilibrium isotope effects are negligible (or perhaps coincidentally compensating). This conclusion was reached by Baird and Aboderin,[5] but on less direct arguments.

Rearrangement of 1-Propyl to 2-Propyl Hydrogen Sulfate. Although 1-propyl hydrogen sulfate is initially formed in 60–98% H_2SO_4, it rearranges cleanly to 2-propyl hydrogen sulfate.

$$CH_3CH_2CH_2OSO_3H \xrightarrow[H_2SO_4]{60\text{–}98\%} (CH_3)_2CHOSO_3H \qquad (1)$$

The half-time for this reaction is about 30 hr in 95% H_2SO_4 at 25°. The rate rapidly decreases in lower acid concentrations so that no rearrangement can be detected at the end of 24 hr in 80% acid. In 30% oleum, the rearrangement is complete within 1 min so that addition of 1-propanol, 2-propanol, or cyclopropane produces only 2-propyl hydrogen sulfate. When reaction 1 was conducted in 95% D_2SO_4, the results were that 1-propyl hydrogen sulfate did not exchange hydrogen for deuterium prior to rearrangement. The product, 2-propyl hydrogen sulfate, wss formed with

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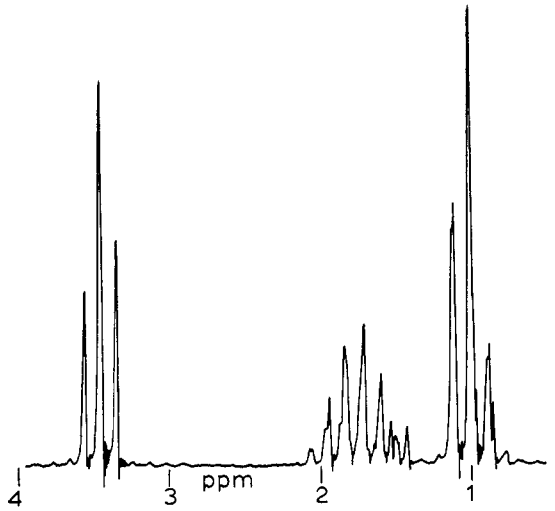


Figure 1. 1-Chloropropane from HCl + cyclopropane (15% $FeCl_3$ as catalyst) at −34°.

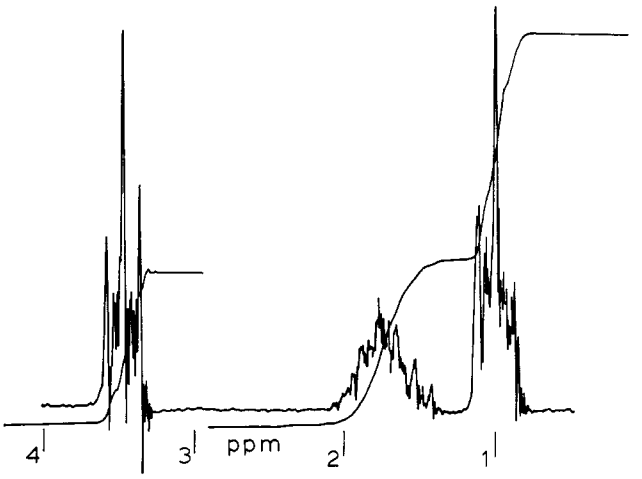


Figure 2. 1-Chloropropane from DCl + cyclopropane (15% $FeCl_3$ as catalyst) at −34°.

the two methyl groups completely converted to CD_3 groups. However, this is not informative because 2-propyl hydrogen sulfate also undergoes complete exchange on the methyl groups within the 2 min required for an nmr measurement. What is informative is that the initial product was $(CD_3)_2CHOSO_3H$ with no exchange on C-2 of the product. The hydrogen on C-2 does undergo a very slow exchange.

Electrophilic Substitution on Cyclopropane. Baird and Aboderin found that cyclopropane underwent direct deuteration in 57% D_2SO_4 to form deuterated cyclopropane.[5] This has been repeated in 92% D_2SO_4 with similar results, but using a different technique. When cyclopropane is introduced under the surface of stirred 92% D_2SO_4 with the surface continuously flushed with dry nitrogen, the 1-propyl hydrogen sulfate contains 1.00 ± 0.05 deuteriums (Table I). Under these conditions, deuterated cyclopropanes are continuously removed. When the reaction is conducted in a closed system, deuterated cyclopropanes form and react so that the average deuterium content of product is increased to 1.5.

Since hydrogen can be exchanged for deuterium by electrophilic attack of D^+ on cyclopropane, it was envisioned that the great variety of electrophilic substitution reactions of benzene would find their counterpart in cyclopropane. A careful search for such monosubstituted products from bromination (Br_2 + $FeBr_3$), acetylation (acetic anhydride or chloride + $AlCl_3$), or nitration ($NO_2^+BF_4^-$ in sulfolane) have all failed.

Alkylation of Deuterated Benzene (c-C_6D_6) with c-$C_3H_6D^+$. Benzene was reported to produce n-propylbenzene when alkylated with cyclopropane in the presence of $AlCl_3$ and other Lewis acids. Under our conditions (1–2% $AlCl_3$ catalyst) and with the advantages of gc and nmr analysis, the product appears to be 70% n-propyl and 30% isopropyl at 25° and 59 and 41% at 45° (Table II). The reaction is most simply formulated as alkylation of benzene by protonated cyclopropane (and isopropyl cation).

When cyclopropane is introduced into deuterated benzene in the presence of 1% $AlCl_3$, moistened with D_2O, both the 2-propyl and isopropyl products contain one deuterium. This deuterium is statistically distributed in both cases and the phenyl group is free of hydrogen. This is the expected result if c-$C_3H_6D^+$ isomerizes to scramble the deuterium and then alkylates benzene. Each alkylation ejects a D^+, which reacts with new cyclopropane to re-form c-$C_3H_6D^+$.

$$D^+ + c\text{-}C_3H_6 \longrightarrow c\text{-}C_3H_6D^+$$

$$c\text{-}C_3H_6D^+ + c\text{-}C_6D_6 \longrightarrow C_6D_5C_3H_6D + D^+$$

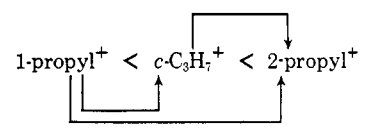
Ratios of Propyl to Isopropyl Products in Alkylation of Aromatics with Cyclopropane. Table II lists these ratios. As the reactivity of the aromatic decreases, the amount of n-propyl decreases and the proportion of isopropyl increases. These results are attributed to a longer accumulated lifetime of c-$C_3H_7^+$ and more opportunity to isomerize to isopropyl cation. The time element indicates that a significant energy barrier exists between these two isomeric $C_3H_7^+$ species.

Table II. Ratios of Isopropyl to n-Propyl Product in the Alkylation of Benzene Derivatives with Cyclopropane (2.5% $AlCl_3$ Catalyst)[a]

Reactant	T, °C	% yields Mono-propyl	% yields Poly-propyl	Relative % n-Propyl	Relative % Iso-propyl
p-Xylene	25	61	33	92	8
Toluene	25	61	22	83	17
Benzene	25	62	28	70	30
	45	67	24	59	41
Chlorobenzene	25	76	12	31	69
o-Dichlorobenzene	25	43	20	<4	>96

[a] The cyclopropane was introduced over a period of 25 min into a fourfold excess of the aromatic. In the runs at 25°, the reaction was allowed to stand an additional 35 min. The run at 45° was worked up after 5 added min.

The Relative Stabilities of $C_3H_7^+$ Ions. The order of stabilities and the essence of the argument for this order is contained in the following diagram.



The data in Table II show that c-$C_3H_7^+$ can isomerize to 2-propyl cation. The reverse reaction has never

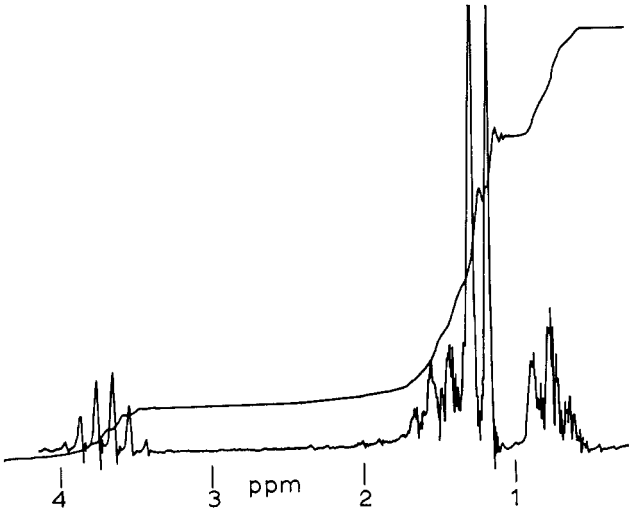


Figure 3. Nmr spectrum of the 2-chlorobutane-4-*d* formed on addition of DCl to methylcyclopropane (no catalyst).

been observed; that is, cyclopropane products are never formed from reactions believed to proceed through 2-propyl cation intermediates.

The relation between 1-propyl and 2-propyl cation is too well known to review. Suffice it to say that 1-propyl isomerizes to 2-propyl, but not the reverse.

The isomerization of 1-propyl cation to $c\text{-}C_3H_7^+$ is indicated by the appearance of cyclopropane in the deamination of propylamine[4] and deoxidation of propanol[3] and the appearance of 1-propanol with scrambled label in the deamination of propylamine.[7] Again the reverse reaction is not known. Although addition of acids to cyclopropane does produce 1-propyl derivatives, such products always exhibit the scrambling of label characteristic of being produced from protonated cyclopropane as shown by the data in Table I.

Relative Stability of 2-Butyl Cation and Protonated Methylcyclopropane. There are several observations that suggest, though not in a decisive fashion, that 2-butyl cation is more stable than protonated methylcyclopropane. In deamination of butylamine, only traces of methylcyclopropane can be detected.[3] Furthermore, the 2-butyl products do not exhibit scrambling of label.[13] These results infer that 2-butyl cation does not isomerize to protonated methylcyclopropane.

Addition of DCl to methylcyclopropane produces only $CH_3CHClCH_2CH_2D$. This is evident both from the 3:1:2:2 ratios of nmr band areas and the nmr splitting patterns (Figure 3). This is the result to be expected if addition of D^+ to methylcyclopropane formed 2-butyl cation directly or *via* a short-lived nonisomerizing protonated methylcyclopropane.

Reactivity of Protonated Cyclopropane. The greater stability of 2-propyl cation over protonated cyclopropane suggests that the latter should be less selective in alkylating toluene. Whereas isopropylation of toluene gives 25–30% *meta* substitution,[14] *n*-propylation with cyclopropane at 25° and 2.5% $AlCl_3$ catalyst gives 46% *ortho*, 38% *meta*, and 16% *para*. This greater than statistical amount of *ortho* or *meta* relative to *para* is curious. These product ratios were obtained after 10-min contact time. Although the products do slowly rearrange, the extent is not significant under the reaction conditions. In addition, the *ortho* disappears most rapidly and isopropyl products form.

Lack of selectivity was also shown in competition experiments at 25°. Toluene reacted 2.0 times faster than benzene at 25°, detected by gc analysis of the reactants.

Protonated cyclopropane is curiously ineffective in abstracting hydride. Treatment of methylcyclohexane with cyclopropane for 4 hr at 25° in the presence of 1% $AlCl_3$ failed to produce propane. Similarly, treatment of benzene, isopentane, and cyclopropane in the molar ratios 4:2:1 for 90 min at 25° in the presence of 2.5% $AlCl_3$ gave only propylbenzene with no trace (by nmr) of *t*-amylbenzene.

Experimental Section

Nmr spectra. These were measured on a Varian A-60A instrument by Ronald D. Brockloff and James F. Espenschied. Tetramethylsilane and tetramethylammonium chloride (3.10 ppm) were used as standards. Small sweep widths were used in measuring band areas in order to give broader bands and more area per band.

Data in Table I. The deuterium distributions were determined from nmr band area relative to each other and to a standard. The nmr spectra for addition of D_2SO_4, CF_3COOD_3, and CH_3COOD were measured directly on the reaction mixtures. For addition of DCl and deuterated benzene, the products were water washed before measuring the nmr spectra.

Data in Table II. The per cent monopropyl product was determined by distillation and weight of residues. In the case of benzene, the ratio of *n*-propyl to isopropyl was determined both by nmr and by gc, the latter being calibrated by authentic mixtures. In the other cases, only nmr was used.

Alkylation of Toluene with Protonated Cyclopropane. The yields of isopropyltoluenes (contained in two gc bands), *o*-propyltoluene, and a *m,p*-propyltoluene mixture were determined by gc on an 18 ft × 0.25 in. column packed with 5% Bentone[15] and 5% diisodecyl phthalate on 45–60 mesh Chromosorb W.[15] Retention times and linear response were checked with authentic samples of *o*, *m*-, and *p*-propyltoluene. These were prepared by reducing the corresponding toluic acids with $LiAlH_4$ in tetrahydrofuran, converting the alcohols to chlorides with Lucas reagent (equimolar $ZnCl_2$ and concentrated HCl), and treating the chlorides with CH_3CH_2MgBr in ether.

The analysis of the *meta* and *para* ratio was accomplished by collecting gc samples and recording the nmr spectrum. Fortunately, the aryl hydrogens appear in two bands, one composed of *m*- and *p*-hydrogens and one composed of just *m*-hydrogen(s). Precise band areas could be secured by recording the spectra at 50-cps sweep width. The spectrum was compared to nmr spectra of authentic mixtures until an exact match was obtained.

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