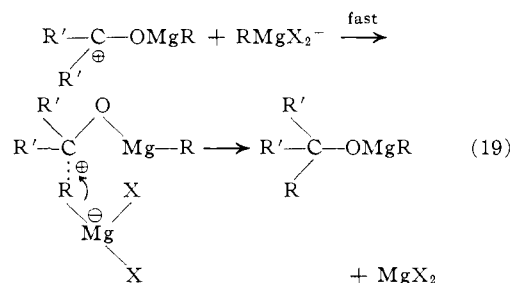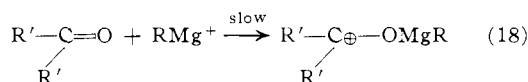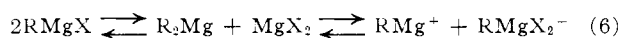stantially faster rate than Grignard compound addition.

Prior coordination of the ketone by MgX_2 followed by R_2Mg addition to the polarized carbonyl group is not probable on the basis that coordination by MgX_2 in the presence of RMgX and R_2Mg is unlikely (for the reasons discussed previously). Also the intermediate product of such an addition ($R_2'RC-OMgX$) does not explain the reduced reactivity of the Grignard after 50% reaction.

Finally, it appears that Grignard compound addition to ketones can also be explained in terms of attacking ionic species.

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \rightleftharpoons RMg^+ + RMgX_2^- \quad (6)$$

$$R'-C=O + RMg^+ \xrightarrow{\text{slow}} R'-C\oplus-OMgR \quad (18)$$
$$\quad\ R' \qquad\qquad\qquad\qquad\quad R'$$

$$R'-C-OMgR + RMgX_2^- \xrightarrow{\text{fast}}$$
$$\quad\ \oplus R'$$

$$\underset{\overset{|}{Mg}}{\underset{\overset{|}{X}}{R'-\underset{\overset{..}{R}\,\overset{\oplus}{)}}{C}}}\ \underset{X}{Mg-R} \longrightarrow R'-\underset{R}{C}-OMgR \quad (19)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad + MgX_2$$

The same arguments justifying RMgX addition also hold for attacking ionic species.

In summary, the composition of Grignard compounds in ether solution appears to be a function of the solvent, as well as the nature of the halogen involved. The composition of "EtMgBr" in tetrahydrofuran, for example, is adequately described by the equilibrium

$$2RMgX \rightleftharpoons R_2Mg + MgX_2$$
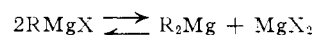
In diethyl ether, however, the composition is expanded to include dimeric species.
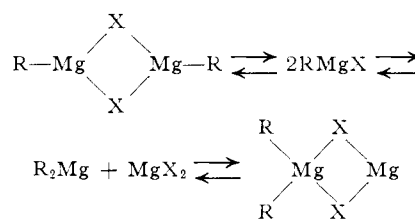
When X = Br and I, association increases with concentration, so that at 0.05 M the species present in solution are predominantly monomeric, whereas at 0.3 M the species present in solution are about one-half monomeric and one-half dimeric. When X = Cl, dimeric species predominate even at 0.05 M.

Conductance data indicate that ionic species such as RMg^+, $RMgX_2^-$, and ion triplets exist in solution, but only to a minor extent.

A new mechanism describing the addition of Grignard compounds to ketones is presented in terms of an attacking monomeric or dimeric RMgX species. All of the pertinent facts reported to date, concerning Grignard compound addition to ketones, can be accounted for in terms of a mechanism involving, in the rate-determining step, ketone displacement of a solvated ether molecule from the attacking Grignard species.

[Contribution from the Department of Chemistry, Whitmore Building, The Pennsylvania State University, University Park, Pennsylvania]

Carbonium Ions. XVII. The Direct Observation of Saturated and Unsaturated Acyl Cations and Their Equilibria with Protonated Acids

By N. C. Deno, Charles U. Pittman, Jr., and Max J. Wisotsky

The equilibria between RCOOH and $RCOOH_2^+$ and between $RCOOH_2^+$ and RCO^+ have been studied in 0–100% aqueous H_2SO_4 and in 0–80% SO_3 in H_2SO_4. The simple aliphatic carboxylic acids have $[RCOOH_2^+]$ equal to $[RCO^-]$ in 10–25% SO_3 and the shift from >90% $RCOOH_2^-$ to >90% RCO^+ occurs within narrow (~4%) ranges of SO_3 concentrations. It is suggested that the equilibrium shifts between RCO^- and $RCOOH_2^+$ can be used to evaluate changes in the activity of H_2O. The acyl cations, RCO^+, may now be regarded as commonplace and familiar chemical species. Their availability in wide variety will be of synthetic interest.

A representative selection of 11 carboxylic acids have been examined by nuclear magnetic resonance (n.m.r.) spectroscopy in 0–100% aqueous H_2SO_4 and 0–80% SO_3 in H_2SO_4. The shift of equilibria from free acid (RCOOH) to protonated acid ($RCOOH_2^+$) and the further shift from $RCOOH_2^+$ to the acyl cation (RCO^+) were evident. These results, along with the work of Olah, reduce acyl cations to commonplace chemical species and reinforce the current viewpoint that such acyl cations have real existence.

Figure 1 shows the changes in n.m.r. band position for solutions of acetic acid in varying concentrations

of SO_3–H_2SO_4–H_2O. Only the band position shifts, indicating that the changes are entirely confined to the carboxyl group. The downfield shift of 0.56 p.p.m. between 50 and 96% H_2SO_4 is of the magnitude expected for simple protonation. More convincing, the shift is half-completed at 77% H_2SO_4 (35°), agreeing with ultraviolet studies which estimated acetic acid to be half-protonated in 74% H_2SO_4 (25°).[1] Similarly, the n.m.r. data for propionic acid indicate it to be half-protonated in 80% H_2SO_4 (35°) in agreement with the

(1) A. R. Goldfarb, A. Mele, and N. Gutstein, *J. Am. Chem. Soc.*, **77**, 6194 (1955).

TABLE I

POSITIONS OF EQUILIBRIA AT ~35° FOR RCOOH ⇌ RCOOH₂⁺
AND RCOOH₂⁺ ⇌ RCO⁺

Acid	% H₂SO₄, [RCOOH] = [RCOOH₂⁺]	% SO₃ in H₂SO₄, [RCOOH₂⁺] = [RCO⁻]
Acetic	77	15% SO₃
Propionic	80	23% SO₃
Isobutyric		16% SO₃
Cyclopropanecarboxylic	82	23% SO₃
Cyclobutanecarboxylic	80	25% SO₃
Cyclohexanecarboxylic		~12% SO₃
2-Butenoic (crotonic)	76	14% SO₃
2-Methyl-2-butenoic (tiglic)		11% SO₃
3-Methyl-2-butenoic	71	0% SO₃ (100% H₂SO₄)
2,4-Hexadienoic (sorbic)	(~71)ᵃ	7% SO₃
Chloroacetic	100	ᵇ

ᵃ Estimated from studies of the ultraviolet spectrum as a function of % H₂SO₄. These studies will be reported in detail in the Ph.D. Thesis of C. U. Pittman, Jr. ᵇ The protonated acid was still dominant in 65% SO₃.

resulting band position of 3.93 p.p.m. (downfield from tetramethylsilane) agrees with the value of 4.02 reported for CH₃CO⁺ in SbF₅.[4,5] Similarly, for propionic acid and its acyl cation, CH₃CH₂CO⁺, the methyl triplet ($J = 7$ c.p.s.) centers at 1.91 and the methylene quartet centers at 4.06 p.p.m. in good agreement with the ranges of 1.8–2.1 and 4.0–4.4 found for CH₃CH₂CO⁺ in different media.[4,5] Less direct evidence is that the band positions of the α-hydrogens are like those of the α-hydrogens in alkenyl cations (2.5–3.5) and (CH₃)₄N⁺ (3.10).[6]

Figure 1 is typical of the curves found for the carboxylic acids. Noteworthy is the narrow range of SO₃ concentrations within which the equilibria shift from >90% RCOOH₂⁺ to >90% RCO⁺. This is generally over a range of 4% in SO₃ concentration. The % H₂SO₄ or % SO₃ at which [RCOOH] is equal to [RCOOH₂⁺] and [RCOOH₂⁺] is equal to [RCO⁺] are summarized in Table I. The n.m.r. band positions

TABLE II

N.M.R. BAND POSITIONS OF RCOOH, RCOOH₂⁺, AND RCO⁺

Acid		RCOOH in 50% H₂SO₄	RCOOH₂⁺ in 96% H₂SO₄	RCO⁺ in 60% SO₃–40% H₂SO₄	Character of band
Aceticᵇ		2.11	2.67	3.93	
Propionic	α-H	2.41	2.94	4.06	Quartet, $J = 7$ c.p.s.
	β-H	1.09	1.37	1.91	Triplet, $J = 7$ c.p.s.
Isobutyric	α-H	2.67	3.18	4.23	Septet, $J = 7$ c.p.s.
	β-H	1.30	1.49	1.90	Doublet, $J = 7$ c.p.s.
Cyclopropanecarboxylic	α-H	1.5	1.8	2.8	Multiplet
	β-H	1.02			Doublet, $J = 6$ c.p.s.
			1.78	2.76	Broad band
Cyclobutanecarboxylic	α-H	3.17	3.56	4.62	Poorly resolved quartet, $J = 8.5$ c.p.s.
	β-H	2.17	2.42	3.13	Complex multiplet, position of most intense peak listed
Cyclohexanecarboxylic	α-H		2.82	4.24	Multiplet
2-Butenoic (crotonic)	α-H	5.70	6.26	6.64	$J = 1$ and 16 c.p.s.
	β-H	7.15	7.57	8.95	$J = 7.5$ and 16 c.p.s.
	γ-H	1.90	2.28	2.68	$J = 1$ and 7.5 c.p.s.
2-Methyl-2-butenoic (tiglic)	α-CH₃	1.72	2.00	2.33	Doublet, $J = 1$ c.p.s.
	β-H		7.84	9.08	Quartet, $J = 7.5$ c.p.s., each component split to a doublet, $J = 1$ c.p.s.
	γ-H	1.79	2.08	2.56	Doublet, $J = 7.5$ c.p.s., each component split to a doublet, $J = 1$ c.p.s.
3-Methyl-2-butenoic	α-H	5.81	6.20	6.56	
	γ-H	2.11	2.44	2.81	
		1.94	2.30	2.75	
2,4-Hexadienoic (sorbic)	ε-H		1.98	(4.31)ᶜ	Doublet, $J = 5.5$ c.p.s.

ᵃ N.m.r. spectra were recorded on a Varian A-60 Mc. instrument. Sample temperature was 35°. The internal standard was (CH₃)₄-N⁺ at 3.10 p.p.m. below (CH₃)₄Si (ref. 6). Before each set of runs, a sample of CHCl₃ plus (CH₃)₄Si was used to check the scale calibration of the instrument. ᵇ There was a significant broadening of the hybrid band in 15–17% SO₃ suggesting that the equilibrium was nearly slow enough to resolve the bands of CH₃CO⁺ and CH₃COOH₂⁺. ᶜ This was measured in 9 (or 13)% SO₃ because the acyl cation was unstable in larger SO₃ concentrations. Although the n.m.r. spectrum has not been completely interpreted, the fact that the acid can be recovered unchanged from solution in 13% SO₃ justifies its inclusion in the table. The spectrum of the protonated acid in 96% H₂SO₄ and the acyl cation in 9% SO₃ are shown in Fig. 2.

value 79% H₂SO₄ (25°) estimated from ultraviolet studies.[2]

The n.m.r. studies show both acetic and propionic acids to be dominantly protonated in 100% H₂SO₄ in agreement with cryoscopic studies.[3]

For acetic acid, a further downfield shift of 1.26 p.p.m. occurs very sharply between 13 and 17% SO₃ in H₂SO₄ (13 to 17% oleum). This is interpreted to be the result of the conversion of CH₃COOH₂⁺ to CH₃CO⁺. The most convincing evidence is that the

for all three species are briefly summarized in Table II.

Substituents that stabilize carbonium ions also stabilize RCOOH₂⁺ with respect to RCOOH. This is understandable in terms of the carbonium representation of RCOOH₂⁺, II, which makes a small contribution to the resonance hybrid. The dominant contribution is of course made by I. The stabilizing effect

(2) J. T. Edward and I. C. Wang, Can. J. Chem., **40**, 966 (1962).

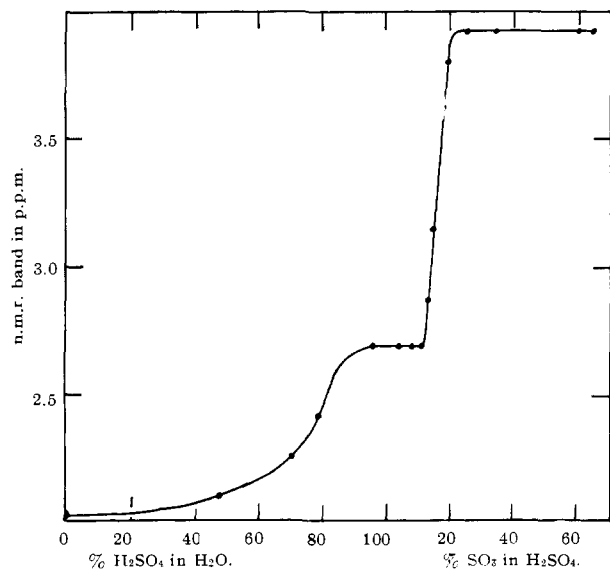(3) L. P. Hammett and A. J. Deyrup, J. Am. Chem. Soc., **55**, 1900 (1933).

(4) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien, and E. B. Baker, ibid., **85**, 1328 (1963).

(5) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, ibid., **84**, 2733 (1962).

(6) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., ibid., **85**, 2991 (1963).

Fig. 2.—N.m.r. spectra of solutions of 2,4-hexadienoic (sorbic) acid in 8% SO_3 in H_2SO_4 (RCO^-, upper curve) and 96% H_2SO_4 ($RCOOH_2^-$, lower curve).

Fig. 1.—Position of the n.m.r. band for solutions of acetic acid in various strengths of H_2SO_4 in H_2O and SO_3 in H_2SO_4 showing the conversion of CH_3COOH to $CH_3COOH_2^-$ to CH_3CO^-.

of substituents in these protonated acids is much reduced from that found in carbonium ions.
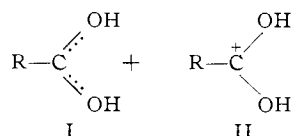
These same substituents that stabilize carbonium ions also stabilize RCO^+ relative to $RCOOH_2^+$. This requires an explanation because the equilibrium formally involves only loss of water

$$RCOOH_2^+ \rightleftharpoons RCO^+ + H_2O \qquad (1)$$
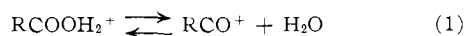
The most obvious interpretation is that more of the positive charge is on carbon in RCO^+ than in $RCOOH_2^+$.

Incidentally, we suggest that the shifts in eq. 1 will be a satisfactory method of estimating activity of H_2O in SO_3–H_2SO_4 and similar systems.

The acyl cations are probably in equilibrium with ketenes

$$RCH_2CO^+ \rightleftharpoons RCH{=}C{=}O + H^+ \qquad (2)$$
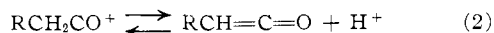
and carbonium ions (the Koch reaction)

$$RCO^+ \rightleftharpoons R^+ + CO \qquad (3)$$
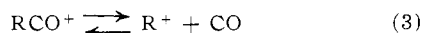
Hydrogen–deuterium exchange studies will elucidate eq. 2. As for eq. 3, similar to the results in SbF_5, $(CH_3)_3CO^+$ in 65% SO_3 rapidly loses CO. After 5 min. at 25°, CO evolution has subsided. The solution at this time shows no trace of the 4.35 p.p.m. band characteristic of $(CH_3)_3C^+$.[7] What is present are the n.m.r. bands of the set of cyclopentenyl cations (the ubications) formed from $(CH_3)_3C^+$ in oleum.[8] Of the acids listed in Table I, only cyclohexanecarboxylic and 2,4-hexadienoic noticeably decomposed in 20 min. at 25°.

Chloroacetic acid solutions exhibited a single band in the n.m.r. spectrum. The position shifted from 4.16 in

H_2O to 4.22 in 50% H_2SO_4 to 4.31 in 90% H_2SO_4. The change is small and so gradual that it is interpreted as attributed to changes in hydrogen bonding energy of the free acid. Between 96% H_2SO_4 and 5% SO_3 the band shifts from 4.37 to 4.59. This would seem to be the result of protonation, since from 5 to 65% SO_3 there is only a small further shift from 4.59 to 4.67 p.p.m.

Concentrations of acyl cations of 25% by weight are readily prepared and it is evident that these have synthetic possibilities. Already we have found that Newman's method of esterification,[9] addition of a solution of the acid in 100% H_2SO_4 to alcohol, formerly thought to be restricted to mesitoic acid and its congeners, is generally extensible to the majority of carboxylic acids by the simple expedient of using 25% SO_3 in H_2SO_4 in place of 100% H_2SO_4. Practically, it is necessary to add RCOOH to ~70% SO_3, and a simple calculation of the H_2O produced will serve to estimate the ratios required to result in an effective SO_3 concentration of 25–30%. The addition of SO_3–H_2SO_4 systems to alcohol causes no trouble providing rapid dispersal methods are used such as we have championed for the addition of H_2SO_4 to 10% aqueous NaOH.[6,8]

A solitary example of equilibria between RCO^+ and $RCOOH_2^+$ had been reported previously. 2,4,6-Trimethylbenzoic (mesitoic) acid was known to form the acyl cation in 100% H_2SO_4 from cryoscopic studies[3] and Schubert and co-workers found $[RCO^+]$ = $[RCOOH_2^+]$ in 97% H_2SO_4.[10] The current n.m.r. study confirms this value. In 60% SO_3, the band positions of the acyl cation are 2.73, 2.60, and 7.41 for o- and p-methyls and m-hydrogens. The analogous values for the protonated acid in 92% H_2SO_4 were 2.43, 2.34, and 7.08. The equilibration of RCO^+ and $RCOOH_2^+$ is slow enough with this acid that the n.m.r. bands of RCO^+ and $RCOOH_2^+$ are independently observed from 93–99.5% H_2SO_4. The n.m.r. spectra indicate RCO^+ to be half-formed at 98% H_2SO_4 and 35°.

(7) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(8) N. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, **86**, 1745 (1964).
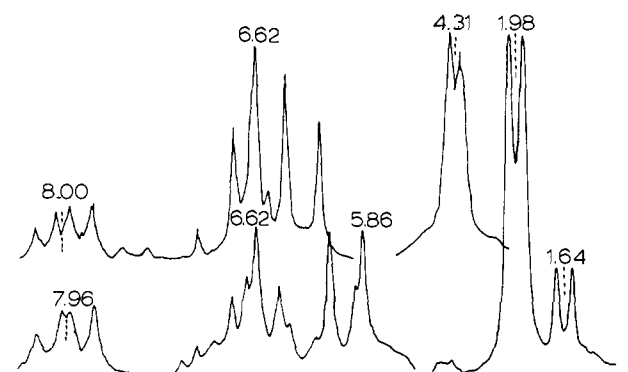
(9) M. S. Newman, *ibid.*, **63**, 2431 (1941).

(10) W. S. Schubert, J. Donohue, and J. D. Gardner, *ibid.*, **76**, 9 (1954).