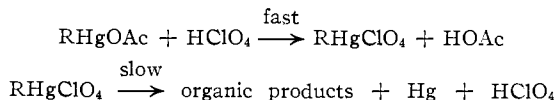


quantity of acid had been added. Indicator studies have shown that when perchloric acid is added to cyclohexylmercuric acetate in acetic acid an instantaneous reaction occurs which eliminates the free acid. The only scheme that can accommodate these facts is



The fact that at the completion of the reaction all the acid had been regenerated is considered conclusive evidence for the scheme.

This method allows the conversion of alkylmercuric acetates to other more ionic salts in solution. The high reactivity of these salts and the influence of the solvent on their stability by coordination, which will be discussed in later papers, does not readily permit their isolation except in the case of primary alkyl mercuric salts.

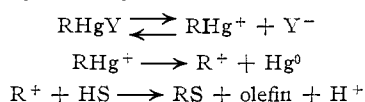
The effect of the anion on the rate of solvolysis indicates that the rate parallels the expected ionization of the salt (Table I). The free energy of

TABLE I
REACTION PARAMETERS FOR THE SOLVOLYSIS OF CYCLOHEXYLMERCURIC SALTS IN ACETIC ACID SOLUTION AT 25°

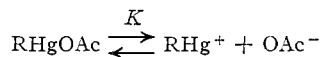
Anion	ΔH^* , kcal./mole	ΔS^* , e.u.	ΔF^* , kcal./mole	$k_{\text{rel.}}$
ClO_4^-	25.3 ± 0.4	10.9 ± 0.9	22.1	1
BF_4^-	$24.5 \pm .2$	$5.0 \pm .5$	23.0	0.193
OTs^-	$25.1 \pm .1$	$3.7 \pm .3$	24.0	0.037
OAc^-	$27.8 \pm .3$	-3.2 ± 1.0	28.8	1.44×10^{-5}
Br^-	Rate too slow to measure.			

activation for the oxygen-containing compounds parallels the ionization of the corresponding acids in acetic acid.⁶ The products of the reaction, $89.5 \pm 1.3\%$ cyclohexene and $10.5 \pm 1.3\%$ alkyl acetate, are independent of the nature of the anion.

Although these results prompted the consideration of a number of possible mechanisms, the simplest involves ionization of salt followed by the cation losing mercury to form a carbonium ion.



To test this carbonium ion mechanism, studies in water were carried out. The acetates are partially ionized in aqueous solution according to the equation



The solvolysis of cyclohexylmercuric acetate follows the expression

$$d \text{ product} / dt = k[\text{RHg}^+]$$

The rate data were treated by a complete analytical expression and exhibited the expected dependence on concentration. With added acetate ion, the rate expression becomes

$$\frac{d \text{ product}}{dt} = k[\text{RHg}^+] = kK \frac{[\text{RHgOAc}]}{[\text{OAc}^-]}$$

(6) S. Bruckenstein and I. M. Kolthoff, *J. Am. Chem. Soc.*, **78**, 2974 (1956).

The value for the equilibrium constant for cyclohexylmercuric acetate agrees within a factor of two with that obtained by calculation of an equilibrium constant from conductivity data for methylmercuric acetate.⁷ Since the alkylmercuric perchlorates are almost completely ionized in water solution, their solvolysis follows the expression

$$d \text{ product} / dt = k[\text{RHg}^+] \text{ and } [\text{RHg}^+] = [\text{RHgClO}_4]$$

In water solution, the solvolysis of cyclohexylmercuric tosylate gives the same kinetics and rate constant as the perchlorate. Of the mechanisms considered, these results are consistent only with the reaction scheme proposed above. Also, over a range of conditions no evidence was found that RHgY directly undergoes reaction.

Extension of this work to a large variety of solvents and alkyl groups has shown this reaction to be entirely general.

Experimental.—The reactions were carried out in most instances at concentrations of 0.02 *M*. The alkyl mercuric perchlorates, tosylates and tetrafluoroborates usually were prepared by adding a stoichiometric amount of the corresponding acid to the alkylmercuric acetate and therefore some of the reactions contained about 0.04 *M* water. Excess acid and water in small amounts had no effect on the rate of reaction.

The reactions were followed by three methods. The alkylmercuric acetates were in some instances treated with bromine ion and the resulting acetate ion titrated with acid. Other alkylmercuric salts were followed by determining the amount of acid generated if the reaction was carried out in a solvent where a convenient indicator system could be devised. The concentration of alkylmercuric salt in some instances was followed by titration with thiocyanate ion by conventional means. The various methods gave identical results. In the case of extremely fast rates, the reaction was quenched with thiocyanate ion and the excess back-titrated with silver ion.

(7) J. L. Maynard and H. C. Howard, *J. Chem. Soc.*, **123**, 960 (1922).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA

FREDERICK R. JENSEN
ROBERT J. OUELLETTE

RECEIVED SEPTEMBER 20, 1961

ORGANOMERCURIALS. IX. THE NATURE OF THE CARBONIUM IONS FORMED IN THE SOLVOLYSIS OF ORGANOMERCURIALS¹

Sir:

In a previous paper,² it was demonstrated that alkylmercuric ions undergo solvolysis reactions in which mercury serves as the leaving group.



This reaction provides a valuable new system for studying solvolytic reactions. Evidence is given in the present paper which indicates that this reaction is less susceptible to nucleophilic attack on carbon than any reaction previously investi-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477 (1961).

gated, that it is probably the first system, investigated kinetically in which non-specifically-solvated primary carbonium ions have been formed in a solvolysis reaction, and that relative to the ground states the central carbon atoms in the transition states bear very large positive charges. Whereas the maximum differences in free energies of activation of solvolytic reactions in acetic acid previously reported for *t*-butyl and methyl compounds is approximately 8 kcal./mole, the difference for the solvolysis of *t*-butyl and methylmercuric salts is approximately 17.5 kcal./mole.

The effect of solvent on the reaction is complex. This is to be expected since some of the more ionizing solvents coördinate with mercury to a large extent. It has been found that with solvents of about the same ionizing power, the reaction occurs more slowly in the more nucleophilic solvent. The results given in Table I probably indicate that in these solvents the interaction between solvent and mercury is the most important effect, and this effect slows the reaction.

TABLE I
PARAMETERS FOR THE REACTION OF CYCLOHEXYLMERCURIC PERCHLORATE IN VARIOUS SOLVENTS AT 25°

Solvent	ΔH^* , kcal./mole	ΔS^* , e.u.	ΔF^* , kcal./ mole	$k_{rel.}$
HOAc	25.3 ± 0.4	10.9 ± 0.9	22.1	1
EtOH	30.3 ± .2	19.6 ± .6	24.5	0.017
MeOH	29.6 ± .4	18.4 ± 1.2	24.1	.030
<i>n</i> -BuOH	30.3 ± .2	19.5 ± 0.6	24.5	.0165
Dioxane	25.3 ± .3	9.9 ± .9	22.4	.60
Acetone	29.1 ± .2	20.5 ± .7	23.0	.204
H ₂ O	28.5 ± .2	17.1 ± .6	23.4	.098

If it is assumed that the degree of coördination of a solvent with mercury is approximately independent of the alkyl group attached to mercury, information regarding the nature of the transition state can be deduced from the data in Table II.

TABLE II
EFFECT OF ALKYL GROUP ON THE SOLVOLYSIS OF ALKYL MERCURIC PERCHLORATES IN WATER AND ACETIC ACID AS SOLVENTS

RH _g ClO ₄ R is	$\Delta H^*_{H_2O} -$ ΔH^*_{HOAc} , kcal./mole	$\Delta F^*_{H_2O} -$ ΔF^*_{HOAc} , kcal./ mole, 25°	$k_{rel. (HOAc)}$ 25°
Me	0.4	0.7	1 ^a
Et	3.0	1.6	1.19 × 10 ³
<i>n</i> -Butyl	3.4	1.8	1.7 × 10 ³
Isopropyl	...	2.0	4.1 × 10 ⁷
<i>sec</i> -Butyl	3.3	1.4	8.1 × 10 ⁷
Cyclohexyl	3.2	1.35	1.3 × 10 ⁸
<i>t</i> -Butyl	6.6 × 10 ¹²

^a $k = 3.1 \times 10^{-12}$ sec.⁻¹. Extrapolated from data at elevated temperature.

The observations that the differences in activation energies for each compound are approximately the same in solvents of widely differing ionizing power and nucleophilicity independent of the number of alkyl groups attached to the central carbon atom, and that the differences in relative rates are very large and approximately proportional to the number of alkyl groups attached to carbon indicate that in the transition states the central carbon

atoms are highly charged and that this charge is not specifically solvated. It is to be expected that solvolysis of alkylmercuric salts will be very sensitive to structural changes and that the carbonium ion intermediates will not be highly selective in their reactions.

The relative rate sequence per alkyl group on carbon is striking: $k_{t-Bu}/k_{i-Pr} = 10^{5.2}$; $k_{i-Pr}/k_{Et} = 10^{4.52}$; $k_{Et}/k_{Me} = 10^{3.07}$. For solvolysis of arylsulfonates in acetic acid (75°) the available relative rates³ are: $k_{i-Pr}/k_{Et} = 10^{1.7}$ and $k_{Et}/k_{Me} = 10^{-0.36}$. By projecting relative rates,⁴ it has been suggested that for limiting solvolysis in formic acid, $k_{t-Bu}/k_{i-Pr} \cong 10^6$. This value is not achieved in acetic acid in the present system. The change per alkyl group on carbon might be comparable. For alkylmercuric salts the ratio in formic acid is $k_{i-Pr}/k_{Et} = 10^{5.3}$. By comparison, for solvolysis of arylsulfonates³ in formic acid the ratio is $k_{i-Pr}/k_{Et} = 10^{2.3}$. Thus, solvent-on-carbon participation is exceedingly low for the production of primary (except for perhaps methyl) and secondary carbonium ions from organomercuric ions.

(3) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952).

(4) A. Streitwieser, *Chem. Revs.*, **56**, 644 (1956).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIFORNIA
FREDERICK R. JENSEN
ROBERT J. OUELLETTE
RECEIVED SEPTEMBER 20, 1961

AN ADDITIVITY RELATION FOR C¹³-PROTON COUPLING IN NUCLEAR MAGNETIC RESONANCE

Sir:

N.m.r. C¹³-proton spin-spin coupling constants have previously been correlated with percentage *s* character of the carbon atomic orbital participating in the C-H bond^{1,2} and the C-H bond length.² For compounds of the type CH₃X, an empirical equation expressing J_{CH} in terms of the effective electronegativity of the substituent and the C-X bond length has also been proposed.² In predicting J_{CH} values of compounds involving various tetrahedral-type carbon atoms of the form CHXYZ, the above-mentioned schemes are not very practicable because, first, one seldom has detailed information concerning small deviations of the percentage *s* character of the carbon atoms and, second, bond lengths are extremely difficult to obtain. The purpose of this note is to draw immediate attention to a simple, but precise, additivity relation for predicting C¹³-proton couplings. The additivity function described here is strongly reminiscent of the well-known additivity relations of molar refractivity and parachor.

It has been found in this laboratory that C¹³-proton coupling constants, for compounds of the type CHXYZ, can be separated into three components according to the equation: $J_{CH} = \zeta_x + \zeta_y + \zeta_z$. In this equation J_{CH} is the C¹³-proton spin-spin coupling constant; components ζ_x , ζ_y and ζ_z are contributions which are associated with substituents X, Y and Z, respectively.

The coupling component for the hydrogen atom

(1) J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

(2) N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).