

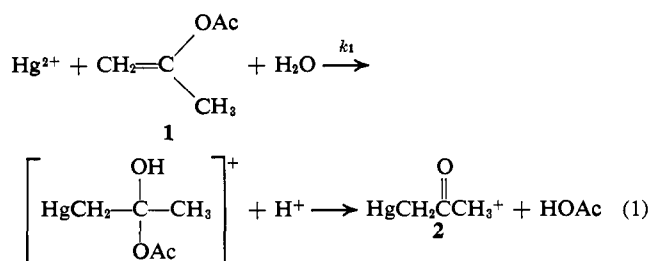
Mercury(II)- and Thallium(III)-Catalyzed Hydrolysis of Isopropenyl Acetate

Peter Abley, James E. Byrd, and Jack Halpern*

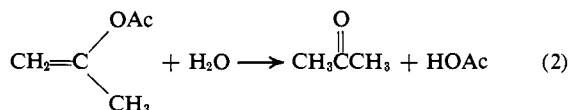
Contribution from the Department of Chemistry, The University of Chicago, Chicago, Illinois 60637. Received August 6, 1971

Abstract: The hydrolysis of isopropenyl acetate in aqueous solution was found to be catalyzed by organomercury(II) and bis(organo)thallium(III) ions, *i.e.*, RHg^+ and R_2Tl^+ , respectively, where $\text{R} = \text{CH}_3\text{COCH}_2$, CH_3 , C_6H_5 , etc. Kinetic and equilibrium measurements are interpreted in terms of an oxymetalation-deoxymetalation mechanism, *i.e.*, $\text{M}^+ + \text{CH}_2=\text{C}(\text{OAc})\text{CH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{MCH}_2\text{C}(\text{OH})(\text{OAc})\text{CH}_3 + \text{H}^+ \rightarrow \text{M}^+ + \text{CH}_3\text{COCH}_3 + \text{HOAc}$ (where $\text{M}^+ = \text{RHg}^+$ or R_2Tl^+). Kinetic measurements on the reaction, $\text{Hg}^{2+} + \text{CH}_2=\text{C}(\text{OAc})\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{HgCH}_2\text{COCH}_3^+ + \text{HOAc}$, and on the corresponding reactions of Tl^{3+} and $\text{TlCH}_2\text{COCH}_3^{2+}$ leading to the formation of $\text{TlCH}_2\text{COCH}_3^{2+}$ and $\text{Tl}(\text{CH}_2\text{COCH}_3)_2^+$, respectively, also are reported.

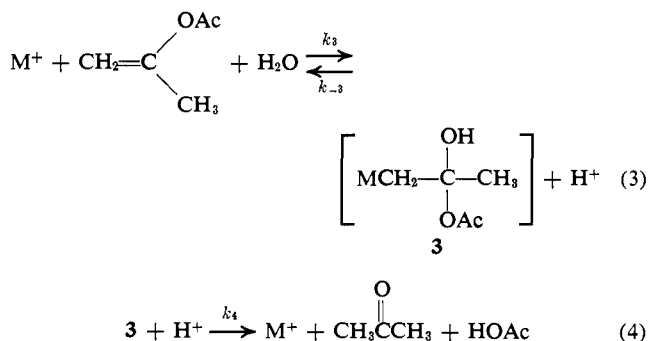
We have recently reported that Hg^{2+} reacts with isopropenyl acetate (1) in aqueous solution to form the mercuriacetone ion (2) according to eq 1,



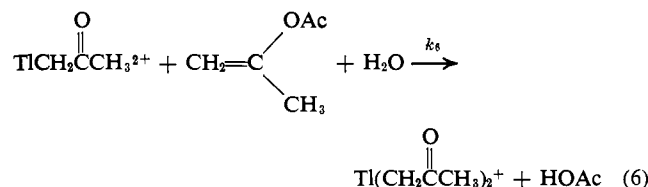
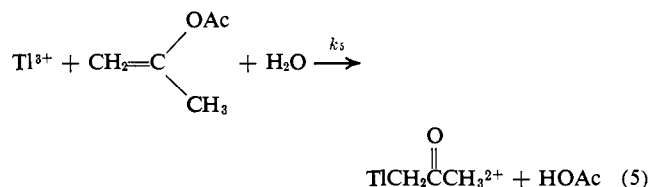
and that 2, in turn, catalyzes the hydrolysis of excess isopropenyl acetate to acetone (eq 2).¹



In this paper we report extensions of these studies which demonstrate that the catalysis of reaction 2 is effected also by other organomercury(II) ions, RHg^+ (where $\text{R} = \text{CH}_3$, C_6H_5 , etc.), as well as by bis(organo)thallium(III) ions, R_2Tl^+ . Kinetic and equilibrium measurements are described, the results of which support the general mechanism depicted by eq 3 and 4



(where $\text{M}^+ = \text{RHg}^+$ or R_2Tl^+), corresponding to that previously proposed for the $\text{HgCH}_2\text{COCH}_3^+$ -catalyzed hydrolysis of isopropenyl acetate. We also report the results of kinetic measurements on reaction 1 and on the corresponding reactions (eq 5 and 6) leading to the



formation of $\text{TlCH}_2\text{COCH}_3^{2+}$ and $\text{Tl}(\text{CH}_2\text{COCH}_3)_2^+$, respectively.

Experimental Section

Materials. The following organomercury and organothallium halides were obtained from Eastman or Alfa Inorganics and recrystallized from methanol: CH_3HgCl , $\text{C}_6\text{H}_5\text{HgCl}$, $p\text{-CH}_3\text{C}_6\text{H}_4\text{-HgCl}$, $(\text{CH}_3)_2\text{TlCl}$, $(\text{C}_6\text{H}_5)_2\text{TlCl}$. $p\text{-ClC}_6\text{H}_4\text{HgCl}$ (mp 238–240°, lit.² mp 240°) and $p\text{-NO}_2\text{C}_6\text{H}_4\text{HgCl}$ (mp 261°, lit.² mp 265°) were synthesized from $p\text{-ClC}_6\text{H}_4\text{NH}_2$ and $p\text{-NO}_2\text{C}_6\text{H}_4\text{NH}_2$, respectively, by the procedure of Nesmeyanov.² $p\text{-NH}_2\text{C}_6\text{H}_4\text{HgCl}$ was prepared from $p\text{-NH}_2\text{C}_6\text{H}_4\text{OAc}$ (Eastman) according to Nesmeyanov.²

Solutions of $\text{HgCH}_2\text{COCH}_3^+$, $\text{TlCH}_2\text{COCH}_3^{2+}$, and $\text{Tl}(\text{CH}_2\text{COCH}_3)_2^+$ were prepared by the stoichiometric reactions of isopropenyl acetate with Hg^{2+} and Tl^{3+} in aqueous perchloric acid solution according to eq 1, 5, and 6, respectively. Solutions of the other organomercury(II) and bis(organo)thallium(III) ions (RHg^+ and R_2Tl^+ , as their perchlorate salts) were prepared from the corresponding halides RHgX and R_2TlX (obtained as described above) by the following procedure. A solution of the halide in aqueous methanol, to which were added an equivalent amount of reagent grade silver perchlorate and sufficient perchloric acid to prevent hydrolysis, was warmed and stirred. The precipitated silver halide was separated by filtration and the filtrate was evaporated at room temperature under reduced pressure with successive additions of water until all the methanol was removed. The resulting aqueous solution was chilled overnight, filtered, and diluted to the desired concentration.

Solutions of mercury(II) perchlorate and thallium(III) perchlorate were prepared by dissolving HgO and $\text{Tl}(\text{OH})_3$ (each of which had been precipitated from an aqueous solution of the corresponding perchlorate salt with ammonia and washed thoroughly with distilled water) in aqueous perchloric acid.

(2) L. G. Makarova and A. N. Nesmeyanov, "The Organic Compounds of Mercury," North-Holland Publishing Co., Amsterdam, 1967, and references therein.

(1) J. E. Byrd and J. Halpern, *Chem. Commun.*, 1332 (1970).

Sodium perchlorate was prepared by neutralizing reagent grade perchloric acid with sodium carbonate and recrystallizing the precipitated salt from distilled water.

Perchloric acid and isopropenyl acetate (Aldrich, >99%) were reagent grade chemicals. Distilled water was used for the preparation of all solutions.

Isolation and Characterization of Products. The products of reaction 1 were characterized by pmr, the product solution having the following spectrum: δ 2.1 (s, 3, HOAc methyl), δ 2.3 (s, 3, CH₃ of 2), δ 3.0 (s, 2, CH₂ of 2). 2 was also isolated as the chloride, CH₃COCH₂HgCl, by addition of sodium chloride to the product solution. The resulting product (mp 103–104°, lit.³ mp 104°) was identical with a sample of CH₃COCH₂HgCl prepared from the reaction of isopropenyl *n*-butyl ether with mercury(II) acetate according to Nesmeyanov.³

The product of reaction 5, *i.e.*, Tl(CH₂COCH₃)₂⁺, exhibited the following pmr spectrum: δ 2.53 (d, 3, $J_{\text{Tl-H}} = 53$ Hz, CH₃), δ 4.44 (two doublets, 2, $J_{205\text{Tl-H}} = 729$ Hz, $J_{203\text{Tl-H}} = 723$ Hz, CH₂); ²⁰⁵Tl: ²⁰³Tl relative abundance ~3:1. Attempts to isolate the acetate, (AcO)₂TlCH₂COCH₃, yielded a rather unstable, light-sensitive product (ir: $\nu_{\text{C=O}}$ (Nujol) 1660 cm⁻¹).

The product of reaction 6, *i.e.*, Tl(CH₂COCH₃)₂⁺, exhibited the following pmr spectrum: δ 2.47 (d, 6, $J_{\text{Tl-H}} = 12.5$ Hz, CH₃; broadened presumably due to unresolved ²⁰³Tl and ²⁰⁵Tl coupled signals), 3.60 (two doublets, 4, $J_{205\text{Tl-H}} = 393$ Hz, $J_{203\text{Tl-H}} = 387$ Hz, CH₂). Addition of sodium chloride to a *ca.* 1 *M* product solution yielded, on cooling, a precipitate of the chloride (CH₃COCH₂)₂TlCl which was separated by filtration, washed successively with chilled water, ethanol, and ether, and dried over P₂O₅ *in vacuo*; mp 180–185° dec; ir $\nu_{\text{C=O}}$ (Nujol) 1685 cm⁻¹. *Anal.* Calcd for C₆H₁₀O₂ClTl: C, 19.36; H, 2.84; O, 9.04; Cl, 10.02. Found: C, 19.37; H, 2.71; O, 9.16; Cl, 10.56.

The course of reaction 2 was followed and the organic products (*i.e.*, acetone and acetic acid) were identified and quantitatively determined by pmr (confirmed by glpc): δ 2.18 (s, 6, acetone), δ 2.10 (s, 3, HOAc methyl).

Kinetic Measurements. The kinetics of reaction 2 were studied by pmr, monitoring the reactant (using the signal at δ 2.15 due to the acetate protons of 1) as well as each of the two products (using the δ 2.18 signal due to the methyl protons of acetic acid). These measurements were made in the nmr spectrometer at 40 ± 1°. Control experiments were performed to determine the contribution from the acid-catalyzed hydrolysis of 1, and, in the few cases where this contribution was significant, an appropriate correction was made; this correction never exceeded 10% of the rate due to the mercury(II)- or thallium(III)-catalyzed reaction.

The kinetics of reactions 1, 5, and 6 were studied spectrophotometrically by monitoring the increases in absorbance accompanying these reactions at 250, 215, and 280 nm, respectively. The kinetics of reaction 4 for several RHg⁺ and R₂Tl⁺ ions, as well as the corresponding equilibrium constants, were also determined spectrophotometrically from the measured absorbance changes in the 270–310-nm regions. All the spectral measurements were performed in a Cary 14 spectrophotometer with a cell compartment thermostated at 25 ± 0.5°. The treatment of the kinetic data for these reactions (as well as of the kinetic data for reaction 2 which is complicated by the accompanying occurrence of reaction 4) will be described later.

Results and Discussion

Kinetics of the Hydrolysis of Isopropenyl Acetate.

Kinetic measurements on reaction 2, performed as described above, typically encompassed the following initial concentration ranges: 0.1 to 0.3 *M* CH₂=C(OAc)CH₃, 0.05 to 0.5 *M* H⁺ (as HClO₄), and *ca.* 1 × 10⁻³ to 1 × 10⁻² *M* RHg⁺ or R₂Tl⁺. The ionic strength was maintained at 1.5 *M* with NaClO₄.

The kinetic results in each case could be accommodated by the general mechanism depicted by eq 3 and 4 and previously reported for the CH₃COCH₂Hg⁺-catalyzed reaction. Both the spectral changes accompanying reaction 3 and the kinetic behavior described below supported the conclusion that under the prevailing reaction conditions the equilibrium of step 3 is rapidly

(3) A. N. Nesmeyanov, I. F. Lutsenko, and N. I. Vereshchagina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 457 (1949).

established compared to the ensuing product-forming step 4. On the basis of this assumption and in view of the large excess of 1 over M⁺ (justifying the neglect of [3] compared to [1]), the following relations may be derived, where $K_3 (=k_3/k_{-3})$ is the equilibrium constant of reaction 3 and [M⁺]_{tot} represents the total (*i.e.*, stoichiometric) catalyst concentration

$$[\text{M}^+]_{\text{tot}} = [\text{M}^+] + [3] \quad (7)$$

$$\frac{[\text{H}^+][3]}{[\text{M}^+][1]} = \frac{[\text{H}^+][3]}{([\text{M}^+]_{\text{tot}} - [3])[1]} = K_3 \quad (8)$$

$$\text{rate} = -d[1]/dt = k_4[3][\text{H}^+] \quad (9)$$

Combining eq 8 and 9 yields

$$\frac{-d[1]}{dt} = \frac{k_4 K_3 [\text{M}^+]_{\text{tot}} [1][\text{H}^+]}{[\text{H}^+] + K_3 [1]} \quad (10)$$

Upon integration, this becomes

$$\frac{1}{k_4 K_3 [\text{M}^+]_{\text{tot}}} \ln \frac{[1]_0}{[1]} + \frac{[1]_0 - [1]}{k_4 [\text{M}^+]_{\text{tot}} [\text{H}^+]} = t \quad (11)$$

where [1]₀ is the initial concentration (*i.e.*, at $t = 0$) of 1. The half-life of the reaction, $t_{0.5}$ (*i.e.*, the time at which [1] = 0.5[1]₀), is, accordingly, given by

$$t_{0.5} = \frac{0.693}{k_4 K_3 [\text{M}^+]_{\text{tot}}} + \frac{[1]_0}{2k_4 [\text{M}^+]_{\text{tot}} [\text{H}^+]} \quad (12)$$

In accord with eq 12, the kinetic measurements yielded linear plots, such as those depicted in Figures 1 and 2, of $t_{0.5}$ vs. [M⁺]_{tot}⁻¹ and of $t_{0.5}$ vs. [H⁺]⁻¹. The slopes of these plots and the intercepts of the latter plots yielded internally consistent values of K_3 and k_4 which are listed in Table I. The values of K_3 and k_4 ,

Table I. Equilibrium and Kinetic Data at 40°^a

M ⁺	K_3	$k_4, \text{M}^{-1} \text{sec}^{-1}$
CH ₃ COCH ₂ Hg ⁺	1.5 ^b	2.5 ^b
CH ₃ Hg ⁺	0.11	0.32
<i>p</i> -CH ₃ C ₆ H ₄ Hg ⁺	0.22	1.05
C ₆ H ₅ Hg ⁺	0.29	1.30
<i>p</i> -NH ₂ C ₆ H ₄ Hg ⁺	0.60	1.42
<i>p</i> -ClC ₆ H ₄ Hg ⁺	0.35	1.45
<i>m</i> -CF ₃ C ₆ H ₄ Hg ⁺	0.44	1.95
<i>p</i> -NO ₂ C ₆ H ₄ Hg ⁺	0.90	3.3
(CH ₃ COCH ₂) ₂ Tl ⁺	14	0.25
(CH ₃) ₂ Tl ⁺	1.0	0.03
(C ₆ H ₅) ₂ Tl ⁺	2.6	0.20

^a Ionic strength maintained at 1.5 *M* with NaClO₄. ^b Unaffected by addition of 0.05 *M* HOAc.

thus determined, could be used, in turn, to simulate the complete rate plots (*i.e.*, plots of [1] vs. t according to eq 11) for the individual kinetic experiments. The agreement between such computed rate plots and the corresponding experimental ones, illustrated in Figure 3 for M⁺ = CH₃COCH₂Hg⁺, is seen to be satisfactory.

Stoichiometry and Kinetics of Reactions 1, 5, and 6. The addition of CH₂=C(OAc)CH₃ (1) to solutions of Hg²⁺ and Tl³⁺ resulted in rapid initial spectral changes which provided quantitative evidence for the formation of CH₃COCH₂Hg⁺, CH₃COCH₂Tl²⁺, and (CH₃COCH₂)₂Tl⁺ in accord with eq 1, 5, and 6, respectively.

The initial spectral changes accompanying the addition of 1 to a solution of Hg²⁺ were in quantitative

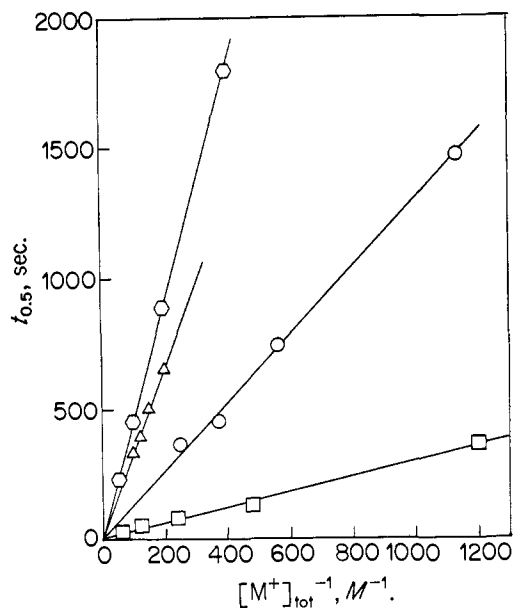


Figure 1. Representative plots of $t_{0.5}$ vs. $[M^+]_{tot}^{-1}$ according to eq 12 (temperature 40° ; ionic strength $1.5 M$; initial $[I]$, 0.1 – $0.2 M$): \square , $CH_3COCH_2Hg^+$ ($0.33 M H^+$); \circ , $(CH_3COCH_2)_2Tl^+$ ($0.2 M H^+$); Δ , $C_6H_5Hg^+$ ($0.05 M H^+$); \diamond , $(C_6H_5)_2Tl^+$ ($0.1 M H^+$).

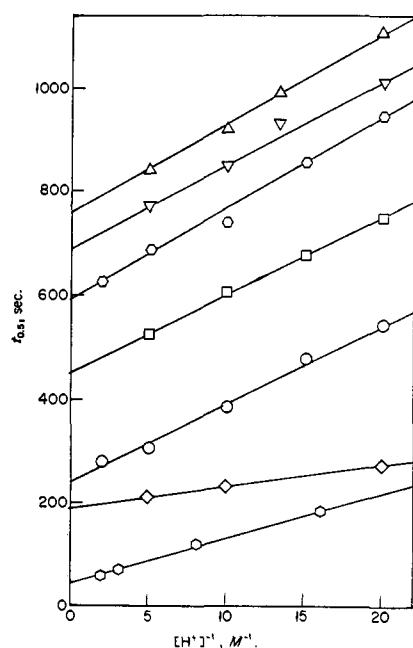


Figure 2. Representative plots of $t_{0.5}$ vs. $[H^+]^{-1}$ according to eq 12: \circ , $CH_3COCH_2Hg^+$ ($4.2 \times 10^{-3} M M^+$, $0.19 M I$); \diamond , $C_6H_5Hg^+$ ($1 \times 10^{-2} M M^+$, $0.1 M I$); \circ , $p\text{-NO}_2C_6H_4Hg^+$ ($1 \times 10^{-3} M M^+$, $0.1 M I$); \square , $p\text{-ClC}_6H_4Hg^+$ ($2.8 \times 10^{-3} M M^+$, $0.1 M I$); \circ , $m\text{-CF}_3C_6H_4Hg^+$ ($1.47 \times 10^{-3} M M^+$, $0.1 M I$); ∇ , $(CH_3)_2Tl^+$ ($3 \times 10^{-2} M M^+$, $0.3 M I$); Δ , CH_3Hg^+ ($5 \times 10^{-2} M M^+$, $0.3 M I$).

agreement with the stoichiometric formation of $CH_3COCH_2Hg^+$ according to eq 1. This is illustrated by Figure 4 which depicts the results of a spectral titration at 275 nm (where the absorption spectrum of $CH_3COCH_2Hg^{2+}$ exhibits a maximum with ϵ $3.6 \times 10^2 M^{-1} \text{ cm}^{-1}$) with an end point at a $[I]:[Hg^{2+}]$ ratio of 1.0 .

Similar spectral changes, associated with the successive stoichiometric formations of $CH_3COCH_2Tl^{2+}$ and $(CH_3COCH_2)_2Tl^+$ [the absorption spectra of which con-

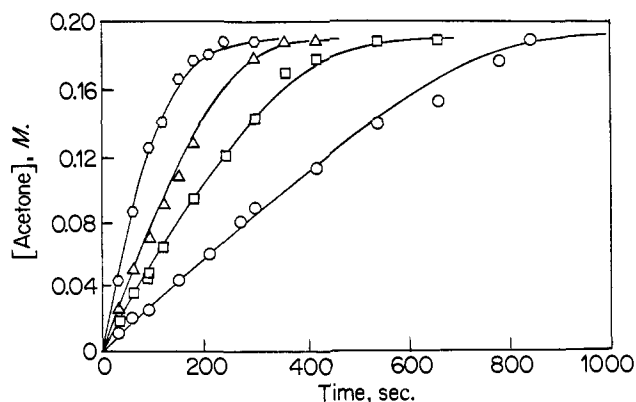


Figure 3. Rate plots for the $CH_3COCH_2Hg^+$ -catalyzed hydrolysis of isopropenyl acetate at 40° : initial $[I]$, $0.19 M$; $[M^+]_{tot} = 4.2 \times 10^{-3} M$. Curves are calculated according to eq 11 using $K_3 = 1.5$ and $k_4 = 2.5 M^{-1} \text{ sec}^{-1}$. Points are experimental data ($[I]_0 = 0.19 M$, $[M^+]_{tot} = 4.2 \times 10^{-3}$): \circ , $3.12 \times 10^{-2} M H^+$; \square , $6.25 \times 10^{-2} M H^+$; Δ , $0.125 M H^+$; \diamond , $0.50 M H^+$.

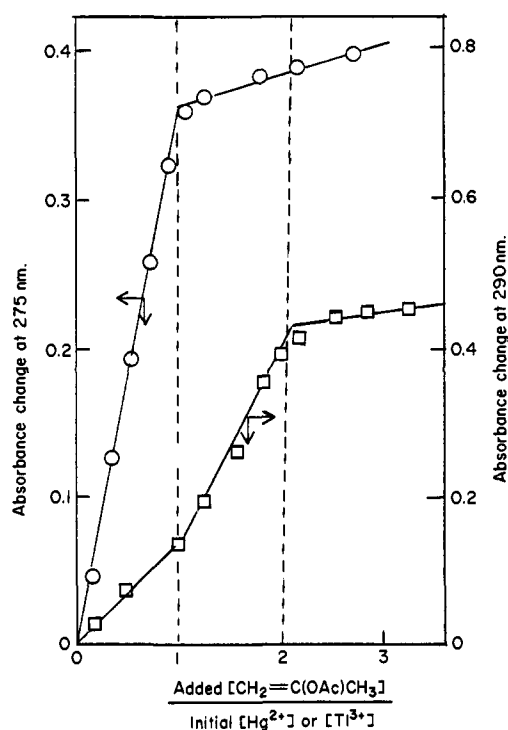


Figure 4. Spectral titrations of $1.0 \times 10^{-3} M Hg^{2+}$ (\circ) and $4.2 \times 10^{-4} M Tl^{3+}$ (\square) with $CH_2=C(OAc)CH_3$ at 275 and 290 nm , respectively ($0.1 M HClO_4$, 1-cm light path).

tain bands centered on 292 nm ($\epsilon_{max} 3.3 \times 10^2 M^{-1} \text{ cm}^{-1}$) and 287 nm ($\epsilon_{max} 8.6 \times 10^2 M^{-1} \text{ cm}^{-1}$), respectively, characterized the addition of **1** to a solution of Tl^{3+} . Figure 4 depicts the results of a spectral titration at 290 nm which reveal end points at $[I]:[Tl^{3+}]$ ratios of $1:1$ and $2:1$, corresponding to the quantitative occurrence of reactions 5 and 6, respectively.

The spectral changes described above were utilized to study the kinetics of reactions 1, 5, and 6, each of which was found to obey a rate law of the form $d[M_i^+]/dt = k_i[M_j][I]$ where $M_1 = Hg^{2+}$, $M_5 = Tl^{3+}$, and $M_6 = CH_3COCH_2Tl^{2+}$, respectively. Kinetic measurements (in which the formation of M_i^+ was monitored spectrophotometrically at wavelengths of *ca.* 275 , 215 , and 280 nm , respectively) were performed under

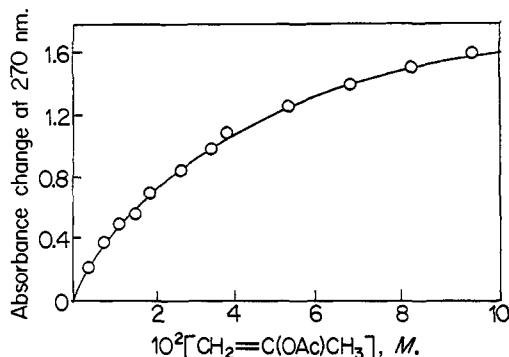


Figure 5. Absorbance change at 270 nm accompanying the addition of $\text{CH}_2=\text{C}(\text{OAc})\text{CH}_3$ to a $1.0 \times 10^{-3} M$ $\text{CH}_3\text{COCH}_2\text{Hg}^+$ solution containing $0.05 M$ HClO_4 . Curve is computed for the equilibrium described by eq 3 using $K_3 = 1.26$.

pseudo-first-order conditions with $[\text{M}]_{\text{initial}} \approx 10^{-4} M$ and $[\text{I}]_{\text{initial}} \approx 5 \times 10^{-4}$ to $3 \times 10^{-3} M$ and $[\text{H}^+] \approx 0.1 M$. These yielded the rate constants, $k_1 = 2.6 \times 10^4 M^{-1} \text{sec}^{-1}$, $k_3 = 1.2 \times 10^2 M^{-1} \text{sec}^{-1}$, and $k_8 = \text{ca. } 5 M^{-1} \text{sec}^{-1}$, all at 25° .

Equilibrium and Kinetics of Reaction 4. The further increases in absorbance, beyond the 1:1 $[\text{I}]:[\text{Hg}^{2+}]$ and 2:1 $[\text{I}]:[\text{TI}^{3+}]$ end points of the spectral titration plots in Figure 4, can be identified with the reversible formation of 3 [*i.e.*, of $\text{CH}_3\text{COCH}_2\text{HgCH}_2\text{C}(\text{OAc})(\text{OH})\text{CH}_3$ and $(\text{CH}_3\text{COCH}_2)_2\text{TI}^{3+}\text{C}(\text{OAc})(\text{OH})\text{CH}_3$, respectively], according to eq 3. The determination of the equilibrium constants for these reactions (*i.e.*, the values of K_3 listed in Table I) from kinetic data has already been described. The spectral changes associated with these reactions provided the basis for an independent direct estimation of K_3 and, hence, for a test of the earlier kinetic interpretation.

At sufficiently low H^+ concentrations ($<0.05 M$) the depletion of 1 due to reaction 4 (for $\text{M}^+ = \text{CH}_3\text{COCH}_2\text{Hg}^+$) proved sufficiently slow, relative to reaction 3, for the initial absorbance change accompanying the latter reaction to be estimated. As demonstrated by Figure 5, the initial absorbance increase at 270 nm, accompanying the addition of 1 to a solution of $\text{CH}_3\text{COCH}_2\text{Hg}^+$, could be fitted to the equilibrium described by eq 3 yielding a value of 1.3 for K_3 at 25° , in reasonable accord with the kinetically determined value of 1.5 at 40° (Table I).⁴

Similar spectral measurements, also at 25° , yielded the K_3 values, 0.35, 0.75, 12, and 1.0 for $\text{M}^+ = \text{C}_6\text{H}_5\text{Hg}^+$, $p\text{-NO}_2\text{C}_6\text{H}_4\text{Hg}^+$, $(\text{CH}_3\text{COCH}_2)\text{TI}^+$, and $(\text{CH}_3)_2\text{TI}^+$, respectively, all in satisfactory accord with the corresponding kinetically determined values in Table I (0.29, 0.90, 14, and 1.0, respectively, at 40°).

Measurement of the rates of the spectral changes just described permitted at least rough estimates to be made of some of the rate constants k_3 and, hence (through the relation $K_3 = k_3/k_{-3}$) of k_{-3} . For $\text{M}^+ = \text{CH}_3\text{COCH}_2\text{Hg}^+$, $\text{C}_6\text{H}_5\text{Hg}^+$, $(\text{CH}_3\text{COCH}_2)_2\text{TI}^+$, and $(\text{C}_6\text{H}_5)_2\text{TI}^+$ the values of k_3 determined in this way at 25° are 2.2, 0.19, 0.7, and $0.21 M^{-1} \text{sec}^{-1}$, respectively. The corresponding values of k_{-3} are 1.5, 0.63, 0.05, and $0.08 M^{-1} \text{sec}^{-1}$, respectively.

(4) Instrumental limitations required the nmr measurements to be made at 40° and the spectral measurements at 25° . Values determined by the two methods are therefore not directly comparable but it is unlikely that the correction due to the temperature difference will be large.

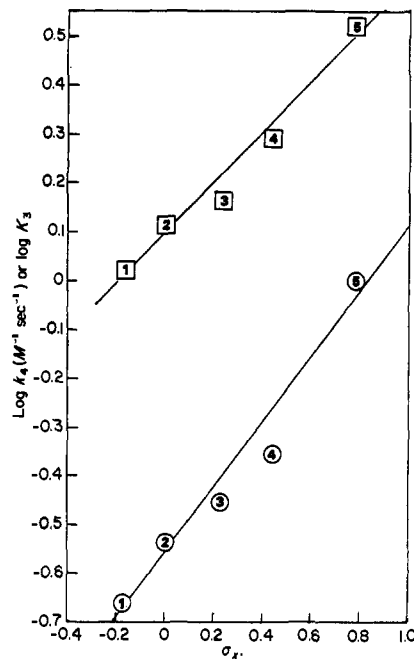


Figure 6. Hammett plots of $\log K_3$ (O) and $\log k_4$ (□) for $\text{X-C}_6\text{H}_4\text{-Hg}^+$: X = (1) *p*- CH_3 , (2) H, (3) *p*-Cl, (4) *m*- CF_3 , (5) *p*- NO_2 .

Mechanisms and Reactivity Trends. The formation of $\text{CH}_3\text{COCH}_2\text{Hg}^+$ has been interpreted in terms of the mechanism depicted by eq 1, involving the hydroxymercuration of $\text{CH}_2=\text{C}(\text{OAc})\text{CH}_3$ as the rate-determining step. The rate law of this reaction, *i.e.*, $-d[\text{Hg}^{2+}]/dt = k_1[\text{Hg}^{2+}][\text{CH}_2=\text{C}(\text{OAc})\text{CH}_3]$, corresponds to that observed for other hydroxymercuration reactions and the value of k_1 , *i.e.*, $2.6 \times 10^4 M^{-1} \text{sec}^{-1}$, is in reasonable accord with values determined earlier for related olefinic compounds (*e.g.*, $3 \times 10^4 M^{-1} \text{sec}^{-1}$ for 2-methylallyl alcohol).⁵ It seems highly likely that the formation of $\text{CH}_3\text{COCH}_2\text{TI}^{2+}$ and $(\text{CH}_3\text{COCH}_2)_2\text{TI}^{2+}$ (eq 5 and 6) occurs through analogous oxythallation-deoxythallation mechanisms. In line with this, it should be noted that the ratio of $k_1/k_3 \sim 2 \times 10^2$ is typical of ratios of rate constants for hydroxymercuration and hydroxythallation of the same olefin, *e.g.*, $\sim 1 \times 10^3$ for propylene,^{5,6} 5×10^2 for 1-penten-4-ol,^{5,7} etc. It should also be noted that the direct mercuration⁸ or thallation of acetone is far too slow to contribute significantly to the observed formation of $\text{CH}_3\text{COCH}_2\text{Hg}^+$ and $\text{CH}_3\text{COCH}_2\text{TI}^{2+}$.

The kinetic evidence described above provides strong support for the mechanism depicted by eq 3 and 4 for the catalyzed hydrolysis of isopropenyl acetate. This mechanism, previously proposed for the $\text{CH}_3\text{COCH}_2\text{Hg}^+$ -catalyzed reaction,¹ also involves an oxymetalation step (eq 3) in which a bis(organo)mercurial or tris(organo)thallium intermediate (for which direct spectral, as well as kinetic, evidence has been provided) is formed. In line with this, the values of k_3 reported above for RHg^+ (2.2 and $0.19 M^{-1} \text{sec}^{-1}$ for $\text{CH}_3\text{COCH}_2\text{Hg}^+$ and $\text{C}_6\text{H}_5\text{Hg}^+$, respectively) are in the range

(5) J. Halpern and H. B. Tinker, *J. Amer. Chem. Soc.*, **89**, 6427 (1967).

(6) P. M. Henry, *ibid.*, **87**, 4423 (1965).

(7) J. E. Byrd, Ph. D. Dissertation, The University of Chicago, 1971.

(8) A. A. Morton and H. P. Penner, *J. Amer. Chem. Soc.*, **73**, 3300 (1951).

of those estimated for the hydroxymercuration of olefinic compounds by other organomercurial ions from measurements on the rates of exchange of olefins with oxymercurials.⁹ Also pertinent to the present theme are recent direct observations of the acid-induced cleavage of diacetylmercury¹⁰ and of the methoxymercuration of an allene by organomercury(II) ions.¹¹

Finally, the results of these studies yield information, not previously available, about the effects of the systematic variation of R in the series of RHg^+ ions examined, both on the equilibrium constant (K_3) of the oxymercuration reaction 3 and on the rate constant (k_4) of the acid-promoted deoxymercuration reaction 4. The data in Table I reveal a marked parallel between the variations of the two constants, each of which appears

to exhibit an inverse dependence on the electron donor strength of R. These trends are reflected in the Hammett plots for the $\text{X-C}_6\text{H}_4\text{Hg}^+$ ions in Figure 6 which yield ρ values of approximately 0.5 for k_4 and 0.6 for K_3 . The direction of the trend for K_3 is readily understood in terms of the influence of increasing electron donation from the R substituent in RHg^+ which is expected to lower the effective positive charge (*i.e.*, electrophilic character) of the Hg atom and, correspondingly, its tendency to form a second mercury-carbon σ bond (*i.e.*, to coordinate a second R⁻ substituent). The origin and significance of the corresponding trends for k_4 , which are expected to be influenced by several compensating factors, are less obvious.

Acknowledgments. Support of this work through grants from the National Science Foundation and from the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

- (9) J. E. Byrd and J. Halpern, *J. Amer. Chem. Soc.*, **92**, 6967 (1970).
 (10) E. Winterfeldt and H. Radunz, *J. Chem. Soc. D*, 374 (1971).
 (11) R. D. Bach, *J. Amer. Chem. Soc.*, **91**, 1771 (1969).

Photolysis of Phenylacetic Acid and Methyl Phenylacetate in Methanol¹

Theodore O. Meiggs and Sidney I. Miller*

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616. Received March 18, 1971

Abstract: Detailed decomposition mechanisms of phenylacetic acid (1) or its methyl ester (2) on photolysis are outlined. The photoproducts (Φ) in methanol of 1 at 26° are CO_2 (0.037), CO (0.013), $(\text{C}_6\text{H}_5\text{CH}_2)_2$ (0.029), $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ (0.005), $\text{C}_6\text{H}_5\text{CH}_3$ (0.002), and of 2 at 31° are CO_2 (0.02), CO (0.028), CH_4 (0.009), $(\text{C}_6\text{H}_5\text{CH}_2)_2$ (0.02), $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{OH}$ (0.01). Both 1 and 2 also yielded substantial quantities of polymer. Following excitation (280–210 nm), the primary processes involve cleavage of the carboxyl function at two bonds: in 1, either benzyl (B) and carboxyl (CO_2H) or phenylacetyl and hydroxyl radicals are formed; in 2, analogous transient pairs are formed. Benzyl radicals recombine to form bibenzyl, react with hydroxymethyl radicals, and may add to the growing acidic polymer. The hydroxyl and methoxyl radicals probably abstract hydrogen from methanol, while the carboxyl species (CO_2H or CO_2CH_3) react with methanol to give formic acid or ester. Reactions that may be ascribed to the solvated electron and hydrogen atoms appear to be insignificant, although the trace of toluene produced from 1 probably arises from the benzyl anion. A general scheme covering the cleavage modes of the carboxyl function *via* homolytic and heterolytic processes is outlined.

Grossweiner and Joschek have surveyed a large number of aromatic molecules for the formation of the solvated electron by flash photolysis.² Subsequently, detailed mechanisms and product patterns were developed for the photochemical behavior of phenols and related derivatives.³ Here, we are concerned with the several routes by which irradiated phenylacetic acid (1) and methyl phenylacetate (2) go to their products.⁴ Although 1 might be regarded as the parent of some acids and a model for others, it turns out that this view could be misleading with respect to the photobehavior of carboxylic acid derivatives in general.⁵

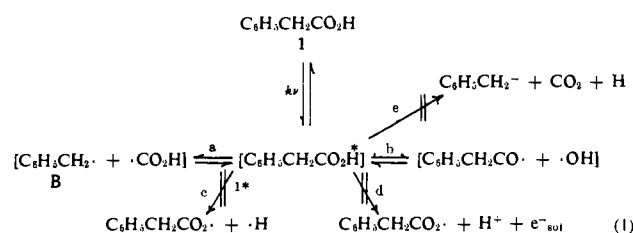
(1) Taken from the Ph.D. Thesis of T. O. M., Illinois Institute of Technology, 1970. Financial support from the Federal Water Pollution Control Administration in the form of a fellowship for T. O. M. and from Public Health Service Grant GM 7021 is gratefully acknowledged.

(2) (a) L. I. Grossweiner and H. I. Joschek, *Advan. Chem. Ser.*, No. 50, 279 (1965); (b) H. I. Joschek and L. I. Grossweiner, *J. Amer. Chem. Soc.*, **88**, 3261 (1966).

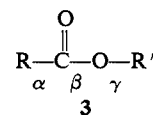
(3) (a) H. I. Joschek and S. I. Miller, *ibid.*, **88**, 3269 (1966); (b) *ibid.*, **88**, 3273 (1966).

(4) T. O. Meiggs and S. I. Miller, to be submitted, material on the properties of the benzyl radical from benzyl phenylacetate and sodium phenylacetate.

(5) (a) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley,



Most simple acids and esters absorb light below 280 nm (>102 kcal/mol), so that enough energy is available to break any of the bonds indicated^{5a}



For simple compounds, *e.g.*, formic acid, acetic acid, methyl formate, and methyl acetate, β photocleavage predominates; there is substantial γ cleavage in acetic acid and a number of other minor paths are generally

New York, N. Y., 1966, pp 427 ff; (b) A. Gilbert, *Photochemistry*, **1**, 430 (1970).