A KINETIC STUDY OF THE CLEAVAGE OF THE IRON—CARBON σ BOND IN η^5-C$_5$H$_5$Fe(CO)$_2$R BY HALOGENATED ACETIC ACIDS

NANCY DE LUCA and ANDREW WOJCICKI *

The McPherson Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210 (U.S.A.)

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Summary

The rates of the reaction of η^5-C$_5$H$_5$Fe(CO)$_2$R (R = alkyl and aryl) with CF$_3$CO$_2$H to give η^5-C$_5$H$_5$Fe(CO)$_2$OC(O)CF$_3$ and RH were investigated in organic solvents, mostly at 25°C, by infrared spectroscopic, manometric and volumetric techniques. When R = alkyl, the cleavage in CH$_2$Cl$_2$ is first order in η^5-C$_5$H$_5$Fe-(CO)$_2$R and first order in the CF$_3$CO$_2$H monomer at acid concentrations $\gtrsim 0.1\,M$, but first order in η^5-C$_5$H$_5$Fe(CO)$_2$R and second order in the CF$_3$CO$_2$H monomer at lower acid concentrations. The dependence of the second-order rate constant on R follows the order C$_6$H$_5$ > CH$_2$Si(CH$_3$)$_3$ (>110) > CH$_3$ (32) > n-C$_4$H$_9$ (15) > C$_2$H$_5$ (11) > CH$_2$C(CH$_3$)$_3$ (6.2) > CH$_2$CH$_2$C$_6$H$_5$ (5.3) > CH(CH$_3$)C$_6$H$_5$ (~1.2) $\gtrsim$ CH$_2$C$_6$H$_5$ (1.0) > CH(CH$_3$)$_2$. The isotope effect, k_H/k_D, for the cleavage of η^5-C$_5$H$_5$Fe(CO)$_2$CH$_3$ by CF$_3$CO$_2$H and CF$_3$CO$_2$D is 4.7. Solvent influence on the rate of the Fe—CH$_3$ bond scission in CH$_2$Cl$_2$, CH$_2$ClCH$_2$Cl and C$_6$H$_6$ is very small. A mechanism is proposed which involves the formation of an Fe-H-OC(O)CF$_3$ hydrogen-bridged 1/1 adduct of the reactants in a reversible step. This adduct then affords [η^5-C$_5$H$_5$Fe(CO)$_2$(R)H][CF$_3$CO$_2$H · O$_2$CCF$_3$] with the assistance of a second molecule of CF$_3$CO$_2$H. Reductive elimination of RH and coordination to iron of CF$_3$CO$_2^-$ complete the reaction. The corresponding cleavage of a given Fe—R bond by CHCl$_2$CO$_2$H is substantially slower than that by CF$_3$CO$_2$H; for the aryl complexes it follows the order R = p-C$_6$H$_4$CH$_3$ > p-C$_6$H$_4$F > C$_6$H$_5$ > p-C$_6$H$_4$Cl, with $\rho \sim -5.4$.

Introduction

Studies in this laboratory over the past several years have focused on the mechanism of reactions of η^5-C$_5$H$_5$Fe(CO)(L)R (L = CO, PR$'_3$, etc.) and related iron complexes with electrophilic reagents [1—5]. In this general context, the kinetics and stereochemistry at metal of the cleavage of the Fe—C σ bonds by SO$_2$ [1—4,6] and HgX$_2$ (X = Cl, Br and I) [4,5,7] have been reported. Stereo-

chemical studies at the α-carbon atom of R of these reactions have also been carried out [8—11].

Acid cleavage of the Fe—C σ bond in η^5-C_5H_5Fe(CO)(L)R has been investigated with regard to stereochemistry at metal [4,7] and at α carbon [12]. Flood and Miles [7] have shown that the reaction of the optically active η^5-C_5H_5Fe-(CO)[$P(C_6H_5)_3$]R (R = CH_3 and C_2H_5) with CF_3CO_2H proceeds with only partial loss of stereochemistry at iron to afford η^5-C_5H_5Fe(CO)[$P(C_6H_5)_3$]OC(O)CF_3. A similar study of the cleavage of the diastereomers of (η^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe-(CO)[$P(C_6H_5)_3$]CH_3 by HI led to the conclusion that the formation of (η^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe(CO)[$P(C_6H_5)_3$]I occurs with net retention of configuration at iron [4]. Both groups proposed a mechanism involving protonation at the metal before reductive elimination of the alkane. A very recent study of the reaction of η^5-C_5H_5Fe(CO)$_2$(cis and trans-4-$C_6H_{10}CH_3$) with CF_3CO_2D and DCl demonstrated that the cleavage proceeds with retention of configuration at α carbon [12], consistent with the aforementioned mechanism.

We now report a kinetic study of the scission of the Fe—C σ bond in η^5-C_5H_5Fe(CO)$_2$R by protic acids to augment the mechanism proposed solely on stereochemical investigations. The acetic acids CF_3CO_2H and $CHCl_2CO_2H$ were selected for this work because of ease of purification and handling, solubility in organic solvents and the propensity to cleave the Fe—C σ bonds to give stable and characterizable products.

Experimental

General procedures

An atmosphere of dry argon or nitrogen was employed routinely in all preparative and kinetic aspects of this work. Especially air or moisture sensitive solutions were prepared in a drybox. Ventron neutral alumina, deactivated with 6% (by weight) distilled water, was used in chromatographic separations and purifications. Mass spectra (MS) were recorded by Mr. C.R. Weisenberger on an A.E.I. Model MS-9 spectrometer or on a DuPont Instruments 21-490 spectrometer connected to a Perkin-Elmer 990 gas chromatograph. Gas chromatography (GC) was performed on a Varian Associates Aerograph Series 1200 instrument using a 10% SE-30 column. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tenn.

Physical measurements

Melting points were obtained on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on Varian Associates A-60A and EM-360L spectrometers using Me$_4$Si as an internal reference. Infrared (IR) measurements were made on Perkin-Elmer Model 337 and Beckman IR-9 spectrophotometers using polystyrene film for calibration. The recorded frequencies are accurate to ±5 and ±1 cm^{-1}, respectively.

Materials

Trifluoroacetic acid, trifluoroacetic acid-d_1 (b.p. 72°C) and trifluoroacetic anhydride (b.p. 39°C), all from Aldrich, were distilled prior to use. The tetra-alkylammonium salts, [(C_2H_5)$_4$N]Cl, [(C_2H_5)$_4$N]O_2CCH$_3$ and [n-C_4H_9)$_4$N]I, all from Eastman, were used as received, except [(C_2H_5)$_4$N]O_2CCH$_3$, which was

recrystallized from acetone and isolated as the tetrahydrate.

Tetraethylammonium trifluoroacetate was prepared by the addition of $[(C_2H_5)_4N]Cl$ (1.80 g, 10.8 mmol) in 20 ml of CH_3OH to a solution of AgO_2CCF_3 (2.21 g, 10.9 mmol), also in 20 ml of CH_3OH. The AgCl was filtered off and the filtrate was concentrated to a milky white oil, which was treated with 50 ml of CH_3OH. The resulting solution was dried over $CaSO_4$ for several days and then filtered. The filtrate was evaporated to dryness to give a quantitative yield of the hygroscopic $[(C_2H_5)_4N]O_2CCF_3$. IR (CH_2Cl_2, cm^{-1}): 1687vs (ν(C=O)), 1171ms, 1142w, 1094w, 695vs (br); ^{1}H NMR (CDCl$_3$, τ): 6.66 (q, J = 7 Hz, CH$_2$), 8.66 (t, J = 7 Hz, CH$_3$).

Dichloromethane and 1,2-dichloroethane were first distilled from P_4O_{10} and then from K_2CO_3, collecting the fractions boiling at 40 and 83°C, respectively. Benzene was distilled at 80°C and stored over molecular sieves (4 Å) or activated neutral alumina. Tetrahydrofuran (THF) was distilled from either LiAlH$_4$ or Na/K alloy at 65°C. Pentane was distilled from CaH$_2$ at 36°C. Other solvents were of reagent grade or equivalent quality and were used without further purification.

Iron alkyls, aryls and related complexes

The following alkyl and aryl complexes η^5-C$_5$H$_5$Fe(CO)$_2$R were prepared by known procedures: R = CH$_3$ [13], CD$_3$ [13], C$_2$H$_5$ [13], CH$_2$C(CH$_3$)$_3$ [1], CH$_2$C$_6$H$_5$ [14], CH(CH$_3$)C$_6$H$_5$ [15], CH(CH$_3$)$_2$ [16], C(CH$_3$)$_3$ [17], C$_6$H$_5$ [18], p-C$_6$H$_4$CH$_3$ [19], p-C$_6$H$_4$Cl [5] and p-C$_6$H$_4$F [20]. η^5-C$_5$H$_5$Fe(CO)$_2$(n-C$_4$H$_9$) was synthesized from Na[η^5-C$_5$H$_5$Fe(CO)$_2$] and n-C$_4$H$_9$Br by using the general method of Piper and Wilkinson [13]. IR (CH$_2$Cl$_2$, cm^{-1}): 2001vs, 1941vs (ν(C≡O)); ^{1}H NMR (CDCl$_3$, τ): 5.36 (s, C$_5$H$_5$), 8.55—9.15 (m, C$_4$H$_9$). η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$Si(CH$_3$)$_3$ and η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$CH$_2$C$_6$H$_5$ were supplied by Dr. L.J. Dizikes.

The trifluoroacetato complex η^5-C$_5$H$_5$Fe(CO)$_2$OC(O)CF$_3$ was prepared by the method of King and Kapoor [21]. IR (CH$_2$Cl$_2$, cm^{-1}): 2065vs, 2021vs (ν(C≡O)). The corresponding dichloroacetato complex, η^5-C$_5$H$_5$Fe(CO)$_2$OC-(O)CHCl$_2$, was obtained from η^5-C$_5$H$_5$Fe(CO)$_2$C$_6$H$_5$ and CHCl$_2$CO$_2$H. A stirred solution of η^5-C$_5$H$_5$Fe(CO)$_2$C$_6$H$_5$ (1.0 g, 3.9 mmol) in 20 ml of benzene was treated dropwise with CHCl$_2$CO$_2$H (0.33 ml, 3.9 mmol) in 2—3 ml of benzene at 25°C. The resulting solution gradually changed color from yellow-orange to red. After 3 h solvent was removed on a rotary evaporator and the residual red oil was dissolved in 1 ml of benzene and chromatographed on alumina. Elution with 65/35 (v/v) benzene/pentane developed a bright orange-red band which gradually started changing color to the dark red of $[\eta^5$-C$_5$H$_5$Fe(CO)$_2]_2$ on slow movement down the column. The band was eluted off with benzene and the solvent was evaporated to yield a dark red oil. The oil was treated with 5 ml of benzene and the mixture was filtered. To the filtrate was added 20 ml of cyclohexane and the resulting solution was concentrated on a rotary evaporator to afford bright red crystals of η^5-C$_5$H$_5$Fe(CO)$_2$OC(O)CHCl$_2$, which were collected by filtration, m.p. 94°C. Yield 0.68 g (57%). Analysis. Found: C, 35.26; H, 2.01; Cl, 23.39%. C$_9$H$_6$Cl$_2$FeO$_4$ calcd.: C, 35.45; H, 1.98; Cl, 23.25%. IR (CH$_2$Cl$_2$, cm^{-1}): 2065vs, 2017vs (ν(C≡O)), 1688 (br) (ν(C=O)); ^{1}H NMR (CDCl$_3$, τ): 4.31 (s, CH), 4.94 (s, C$_5$H$_5$); MS (m/e): 304 (P^+, rel. int. 1.5), 276 ((P—CO)$^+$, rel. int. 15.8), 248 ((P—2 CO)$^+$, rel. int. 24.9), 121 (C$_5$H$_5$Fe$^+$, rel. int. 100).

General kinetic procedures

The kinetic studies of the reactions between η^5-$C_5H_5Fe(CO)_2R$ and the halogenated acetic acids were carried out in a round-bottom flask fitted with a side-arm for gas inlet-outlet. The neck of the flask was sealed with a serum cap, and the flask was wrapped in aluminum foil for protection from light. A solution under argon of freshly chromatographed η^5-$C_5H_5Fe(CO)_2R$, generally in CH_2Cl_2 (CH_2ClCH_2Cl and C_6H_6 were also used), was prepared in the flask, which was then placed in a constant-temperature bath. After thermal equilibrium had been reached, first a small amount of $(CF_3CO)_2O$ (added only when the acid was CF_3CO_2H; about 10% of the volume of CF_3CO_2H) and then 0.10—1.00 ml of the halogenated acetic acid were injected into the flask with a syringe. The use of metal and Teflon syringe needles led to the same rate results; consequently, both were employed in this study. Following the addition of the acid, the solutions were kept in the thermostated bath ($\pm 0.1°C$), generally at $25.0°C$, with magnetic stirring.

(A) Measurements by infrared spectroscopy. Rates of the reactions were for the most part determined by following the disappearance of the lower frequency CO stretching absorption, $\nu_{as}(C\equiv O)$, of the iron-alkyl or -aryl complex (at 1964—1932 cm^{-1} in CH_2Cl_2) or the appearance of the higher frequency CO stretching absorption, $\nu_s(C\equiv O)$, of the iron-acetato product (at 2065 cm^{-1} in CH_2Cl_2) on a Beckman Model IR-9 spectrophotometer. Absorbance readings of the appropriate $\nu(C\equiv O)$ were made on the solution by withdrawing samples with a syringe at various time intervals. Matched infrared cells of various thickness (0.06—2.0 mm) were employed.

All reactions were run under pseudo-first-order conditions, with the concentration of the acid in at least a tenfold excess over that of the iron complex. They were generally followed for three or more half-lives.

Beer's law has previously been shown to hold for the $\nu_{as}(C\equiv O)$ absorption of several η^5-$C_5H_5Fe(CO)_2R$ complexes in the concentration range 2×10^{-3} to 5×10^{-2} M in THF [5]. It was assumed to be valid for the iron-alkyl, -aryl and -acetato complexes in the solvents used in this study.

(B) Manometric measurements. This technique was used to measure the rate of the formation of CH_4 in the cleavage of η^5-$C_5H_5Fe(CO)_2CH_3$ by CF_3CO_2H, especially under fast-reaction conditions ($t_{1/2} \lesssim 3$ min). Either the iron complex or the acid was in at least a tenfold excess over the other reactant. Concentrations of the reactant present in excess were approximately 0.9 M η^5-C_5H_5Fe-$(CO)_2CH_3$ and 0.03—0.2 M CF_3CO_2H.

The apparatus consisted of a reaction flask, described above, which was attached by means of a three-way stopcock to a mercury-filled manometer and to another three-way stopcock connected to a source of vacuum and an argon inlet. The entire system, containing a solution of η^5-$C_5H_5Fe(CO)_2CH_3$ with added $(CF_3CO)_2O$, was thoroughly flushed with argon and evacuated to ca. 550 torr. A sample of CF_3CO_2H was then syringed into the flask and measurements of pressure were taken as often as necessary (intervals $\gtrsim 15$ sec). Generally, during the initial 2—3 min of reaction, pressure changes were small owing to the dissolution of methane (solubility = ca. 0.3—0.5 ml of CH_4/ml of solvent for solvents used in this study [22]). The pressure was measured until a constant value, P_∞, was obtained (usually within 4—5 h).

(C) Volumetric measurements. Some cleavage reactions of η^5-$C_5H_5Fe(CO)_2CH_3$ (ca. 4×10^{-3} M) with a tenfold excess of CF_3CO_2H were followed by measuring the volume of the liberated CH_4.

The apparatus for these experiments was similar to that described elsewhere [23,24] and incorporated a gas buret with a pressure-equalizing bulb. The buret was connected to a thermostated reaction flask which contained a solution of η^5-$C_5H_5Fe(CO)_2CH_3$ with added $(CF_3CO)_2O$ under argon. The acid was then syringed into the flask and the volume readings were taken as needed until evolution of gas ceased. The amount of gas collected was found to be in good agreement with that calculated for the release of one mole of CH_4 per mole of η^5-$C_5H_5Fe(CO)_2CH_3$.

Treatment of data

From the infrared spectroscopic data pseudo-first-order rate constants, k_{obs}, were obtained by graphing $-\ln(A - A_\infty)$ vs. time where A is the absorbance of η^5-$C_5H_5Fe(CO)_2R$ at any time of the reaction and A_∞ is the absorbance of the alkyl complex at infinite time. Since all cleavage reactions went to completion, A_∞ is zero. Alternatively, $-\ln(A'_\infty - A')$ vs. time was plotted when the appearance of the iron-acetato product was monitored.

Data from the manometric and volumetric kinetic experiments where the acid was in at least a tenfold excess over η^5-$C_5H_5Fe(CO)_2CH_3$ were treated in a similar fashion. This will be considered further in the Results section.

Results

Stoichiometry and products

Reactions of the alkyl and aryl complexes η^5-$C_5H_5Fe(CO)_2R$ with $CH_xX_{3-x}CO_2H$ ($X = F$, $x = 0$; $X = Cl$, $x = 1$) in CH_2Cl_2, CH_2ClCH_2Cl or C_6H_6 at ambient temperatures proceed according to the equation

$$\eta^5\text{-}C_5H_5Fe(CO)_2R + CH_xX_{3-x}CO_2H \rightarrow \eta^5\text{-}C_5H_5Fe(CO)_2OC(O)CH_xX_{3-x} + RH$$

$$(1)$$
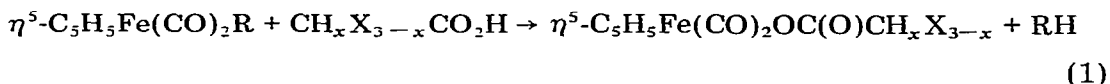
Infrared spectra in the $\nu(C\equiv O)$ region of the reaction solutions show that, except as indicated below, the iron-acetato complexes are formed cleanly as the only iron carbonyl products. * Quantitative isolation of these complexes was precluded by their decomposition in the course of chromatography on alumina to give $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$. The trifluoroacetato complex, η^5-$C_5H_5Fe(CO)_2OC(O)CF_3$, was observed also to decompose on prolonged (ca. 24 h) storage in CH_2Cl_2 solution; again the iron dimer was the metal carbonyl product. Identification of the acetato complexes was accomplished either by comparison of the species isolated from the reaction mixture with an authentic sample prepared by the literature procedure (for η^5-$C_5H_5Fe(CO)_2OC(O)CF_3$ [21]) or by chemical

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* In contrast, two pathways have been reported [25] for the reaction of $Mn(CO)_5C_6H_5$ with hydrogen halides (HX):

$$Mn(CO)_5C_6H_5 + HX \rightarrow Mn(CO)_5X + C_6H_6$$

and

$$Mn(CO)_5C_6H_5 + HX \rightarrow Mn(CO)_5H + C_6H_5X$$
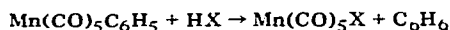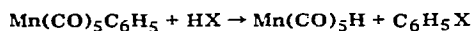
analysis in conjunction with the infrared, ^{1}H NMR and mass spectral data (for η^5-C$_5$H$_5$Fe(CO)$_2$OC(O)CHCl$_2$).

In several cleavage reactions the organic product, RH, was identified by various spectroscopic techniques. Thus, the gas liberated in the reaction of η^5-C$_5$H$_5$Fe-(CO)$_2$CH$_3$ with excess CF$_3$CO$_2$H in CH$_2$Cl$_2$ was characterized by both infrared spectroscopy and mass spectrometry as CH$_4$; no other hydrocarbon was observed. Similarly, the mass spectrum of the gas collected when η^5-C$_5$H$_5$Fe-(CO)$_2$C$_2$H$_5$ reacted with CF$_3$CO$_2$H in CH$_2$Cl$_2$ showed the presence of C$_2$H$_6$ as the only product.

Reactions of each of η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$Si(CH$_3$)$_3$ and η^5-C$_5$H$_5$Fe(CO)$_2$C$_6$H$_5$ with excess CF$_3$CO$_2$H (neat and in CDCl$_3$, respectively) were examined by ^{1}H NMR spectroscopy. Both went cleanly to completion as evidenced by the spectra which consisted of the following singlet resonances: τ -1.70 (OH of CF$_3$CO$_2$H), 4.88 or 4.95 (C$_5$H$_5$ of η^5-C$_5$H$_5$Fe(CO)$_2$OC(O)CF$_3$), as well as 10.00 for the former reaction (Si(CH$_3$)$_4$) and 2.69 for the latter reaction (C$_6$H$_6$). The relative intensities were in accord with the expected 1/1 molar ratio of the two products in each case.

Cleavage by CHCl$_2$CO$_2$H (fivefold excess) of each of η^5-C$_5$H$_5$Fe(CO)$_2$C$_6$H$_4$CH$_3$-p, η^5-C$_5$H$_5$Fe(CO)$_2$C$_6$H$_4$F-p and η^5-C$_5$H$_5$Fe(CO)$_2$C$_6$H$_4$Cl-p in CDCl$_3$ was also studied by ^{1}H NMR spectroscopy. In addition to unreacted acid (singlets at τ -1.71 and 3.91: OH and CHCl$_2$, respectively), the spectra showed η^5-C$_5$H$_5$Fe(CO)$_2$OC-(O)CHCl$_2$ (singlets at τ 4.31 and 4.94: CHCl$_2$ and C$_5$H$_5$, respectively) and the appropriate substituted benzene: C$_6$H$_5$CH$_3$ (τ 2.86s and 7.68s), C$_6$H$_5$F (τ 2.89m) or C$_6$H$_5$Cl (τ 2.74 (br)). Again, the relative intensities confirmed that the products of each reaction formed in a 1/1 ratio.

Three of the investigated complexes exhibited slow and/or more complicated behavior during cleavage. After the reaction of 0.34 M η^5-C$_5$H$_5$Fe(CO)$_2$CH$_2$C$_6$H$_5$ with ca. 2.5 M CF$_3$CO$_2$D in CH$_2$Cl$_2$ had been carried out for 2.3 h, the solvent and other volatile matter were removed under reduced pressure. The collected liquid was shown by GC to consist of CH$_2$Cl$_2$, trifluoroacetic acid and toluene. A mass spectrum revealed the presence of both toluene-d_1 and toluene-d_2. The nonvolatile residue was chromatographed on alumina, yielding unreacted benzyl complex, η^5-C$_5$H$_5$Fe(CO)$_2$OC(O)CF$_3$ and [η^5-C$_5$H$_5$Fe(CO)$_2$]$_2$ from decomposition of the trifluoroacetato complex on the column.

Addition of excess (fivefold to tenfold) CF$_3$CO$_2$H to a solution of η^5-C$_5$H$_5$Fe-(CO)$_2$CH(CH$_3$)$_2$ in CH$_2$Cl$_2$ produced a pale green color of unknown origin which persisted for ca. 0.5 h. The reaction was monitored by infrared spectroscopy and showed only slight formation of η^5-C$_5$H$_5$Fe(CO)$_2$OC(O)CF$_3$ in 5 h. Extended reaction times (ca. 24 h) led to considerable decomposition, presumably owing to the relative instabilities of η^5-C$_5$H$_5$Fe(CO)$_2$CH(CH$_3$)$_2$ and η^5-C$_5$H$_5$Fe(CO)$_2$OC(O)CF$_3$ in solution.

The alkyl η^5-C$_5$H$_5$Fe(CO)$_2$C(CH$_3$)$_3$ also displayed what appeared to be a more complicated reaction with CF$_3$CO$_2$H. Addition of excess CF$_3$CO$_2$H to a CDCl$_3$ solution of η^5-C$_5$H$_5$Fe(CO)$_2$C(CH$_3$)$_3$ produced a transient green color which turned to a deep red on thorough mixing of the reactants. Only very broad signals were observed in the ^{1}H NMR spectrum of this solution, presumably owing to the presence of paramagnetic impurities. An examination by infrared spectroscopy of a solution containing η^5-C$_5$H$_5$Fe(CO)$_2$C(CH$_3$)$_3$ and CF$_3$CO$_2$H (1.9 M,

ca. tenfold excess) in CH_2Cl_2 showed, within 4 min of the addition of the acid, $\nu(C{\equiv}O)$ absorptions at 2128, 2075(br), 2025, 1993 and 1932 cm^{-1}. The two strong bands at 1993 and 1932 cm^{-1} are due to $\eta^5\text{-}C_5H_5Fe(CO)_2C(CH_3)_3$, whereas the weaker ones at ca. 2075 and 2025 cm^{-1} derive from the presence of $\eta^5\text{-}C_5H_5Fe(CO)_2OC(O)CF_3$. The absorptions at 2128 and, presumably, ca. 2075 cm^{-1} are best assigned to an unknown cationic iron dicarbonyl species. The spectrum was monitored for ca. 15 h, during which time the bands at 1993 and 1932 cm^{-1} decreased in intensity whereas those at 2070 and 2025 cm^{-1} gained intensity. After 15 h, only a weak absorption at 2128 cm^{-1} and strong absorptions at 2070 and 2025 cm^{-1} were discernible. Chromatography of the solution on alumina afforded $[\eta^5\text{-}C_5H_5Fe(CO)_2]_2$, from decomposition of $\eta^5\text{-}C_5H_5Fe(CO)_2OC(O)CF_3$ on the column, as the sole iron carbonyl product.

Kinetic determinations

(A) Cleavage by CF_3CO_2H. Kinetic data were obtained by infrared spectroscopy (as well as manometrically and volumetrically when R = CH_3) for the reaction in equation 1 (with X = F and $x = 0$) under pseudo-first-order conditions, with CF_3CO_2H in a tenfold excess over $\eta^5\text{-}C_5H_5Fe(CO)_2R$, in CH_2Cl_2 at 25°C. The reaction mixtures also contained $(CF_3CO)_2O$, introduced as a precaution against the presence of adventitious H_2O. Control experiments had established that the added anhydride does not affect the rate of the cleavage reaction. Moreover, no reaction was detected between equimolar amounts of $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$ and $(CF_3CO)_2O$ in dry CH_2Cl_2 at 25°C over a period of 4 days.

The kinetic data are consistent with the rate law

$$-\frac{d[\eta^5\text{-}C_5H_5Fe(CO)_2R]}{dt} = k_{obs}[\eta^5\text{-}C_5H_5Fe(CO)_2R] \tag{2}$$

Good linear plots of $-\ln(A - A_\infty)$ vs. time were obtained in all cases, with the slope equal to k_{obs}, where

$$k_{obs} = k_{n+1}[CF_3CO_2H]^n \tag{3}$$

A typical plot is shown in Figure 1 for $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$.

The determination of n, the order of the reaction in acid, is complicated by the association of CF_3CO_2H in solution. Studies on solutions of CF_3CO_2H in organic solvents [26] have led to the conclusion that the only important species present are the monomer and cyclic dimer, the association equilibrium being

$$2\,CF_3CO_2H \rightleftharpoons (CF_3CO_2H)_2 \tag{4}$$

The dimerization constnat, K_D, for CF_3CO_2H,

$$K_D = \frac{[(CF_3CO_2H)_2]}{[CF_3CO_2H]_M^2} \tag{5}$$

has been determined at 25°C in several solvents [26], including CH_2ClCH_2Cl (1.5 ± 0.4 M^{-1}), C_6H_6 (2.6 ± 0.9 M^{-1}) and CCl_4 (149 ± 19 M^{-1}), but, to the best of our knowledge, not in CH_2Cl_2.

Since CH_2Cl_2 and CH_2ClCH_2Cl have similar solvent properties and comparable dielectric constants (ϵ = 8.93 and 10.36, respectively, at 25°C [27]), we
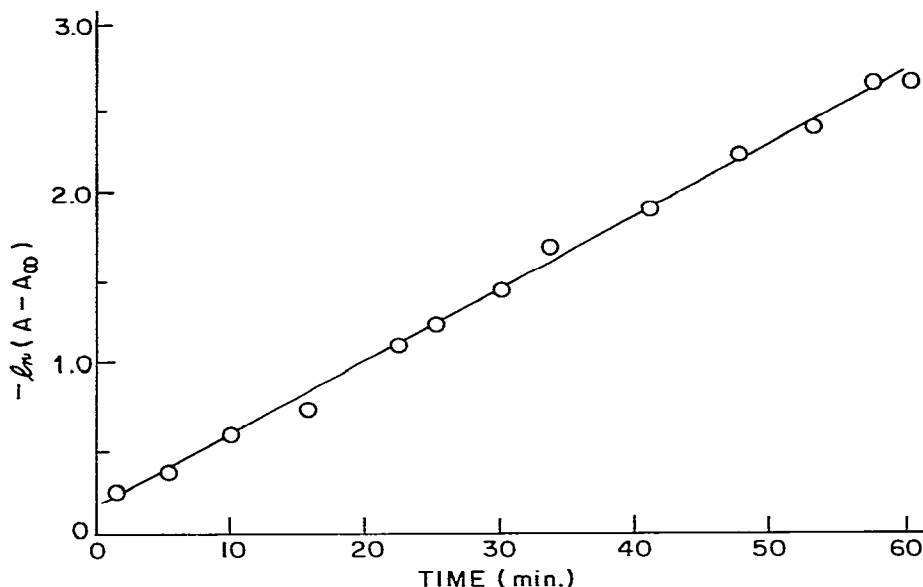
Fig. 1. A typical plot of infrared spectroscopic data for the cleavage of η^5-$C_5H_5Fe(CO)_2CH_3$ by a tenfold excess of CF_3CO_2H in CH_2Cl_2 at $25°C$.

have taken the dimerization constant for CF_3CO_2H in CH_2Cl_2 at $25°C$ to be also $1.5\ M^{-1}$. By using this value, the initial concentration of the monomer, $[CF_3CO_2H]_M$, was calculated for each kinetic run. Plotting k_{obs} vs. $[CF_3CO_2H]_M$ for the various runs with η^5-$C_5H_5Fe(CO)_2CH_3$ affords a straight line at the higher acid concentrations, indicating first-order dependence on the acid monomer in that region. However, the graph begins to slope downward with decreasing $[CF_3CO_2H]_M$ at the lower acid concentrations. An alternative way of graphing these data is based on the logarithmic form of equation 3, i.e.,

$$\ln k_{obs} = \ln k_{n+1} + n \ln[CF_3CO_2H]_M \tag{6}$$

Plotting $\ln k_{obs}$ vs. $\ln[CF_3CO_2H]_M$, as illustrated in Figure 2, shows the slope, n, at the higher acid concentrations to be essentially equal to 1. Hence the cleavage reaction is first order in the monomer acid at $[CF_3CO_2H]_a \gtrsim 0.1\ M$. * However, at the lower acid concentrations the curve slopes upward, indicating that the order of the reaction with respect to $[CF_3CO_2H]_M$ is greater than 1. The curve approaches, but does not reach, a slope of 2. ** It is further noteworthy that a plot of k_{obs} vs. $[(CF_3CO_2H)_2]$ lacks linearity over the range of the acid concentrations employed.

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* The apparent acid concentration, $[CF_3CO_2H]_a$, is the sum of $[CF_3CO_2H]_M$ and $1/2[(CF_3CO_2H)_2]$. At $[CF_3CO_2H]_a = 0.1\ M$, the acid is 80% monomer.

** A referee has expressed concern that the curvature in Figure 2, and therefore our entire argument for the mechanism of the cleavage, rests on uncertain grounds. This is because the value of K_D for CF_3CO_2H is an estimated one, and as such it may well be in error. In order to ascertain how a reasonable error in K_D would affect the plot in Figure 2, we considered CF_3CO_2H to be present exclusively as the monomer. A plot of $\ln k_{obs}$ vs. $\ln[CF_3CO_2H]_M$ constructed on this basis exhibits a curvature similar to that in Figure 2. We therefore conclude that even if the K_D employed in our calculations in somewhat in error, the essential mechanistic conclusions remain unaltered *** (although, of course, the rate constants will change somewhat). For a further consideration of this point see Figure 4 and the derivation of the appropriate equations in the text.

*** K_D would have to be appreciably higher than the assumed value of $1.5\ M^{-1}$ for our conclusions to become invalid. We consider such a situation rather unlikely.
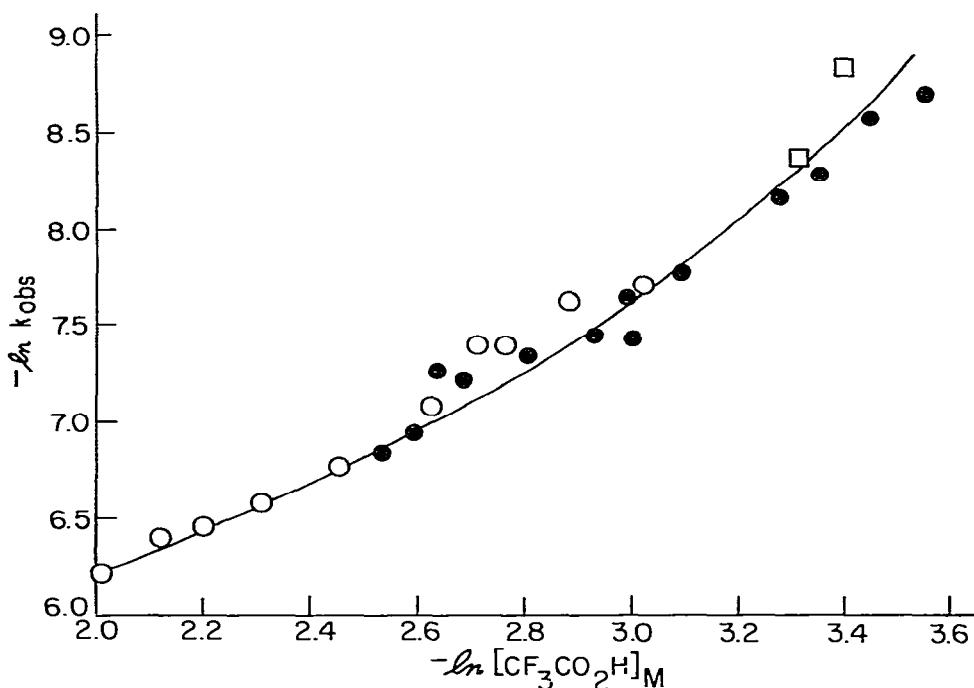
Fig. 2. Cleavage of η^5-$C_5H_5Fe(CO)_2CH_3$ by a tenfold excess of CF_3CO_2H in CH_2Cl_2 at 25°C. The data were obtained o manometrically, ● spectroscopically (infrared) and □ volumetrically.

The order of the reaction with respect to the acid at the lower concentrations can be elucidated by examination of the manometric data for the cleavage of ca. 0.86 M η^5-$C_5H_5Fe(CO)_2CH_3$ with a tenfold deficiency of CF_3CO_2H. A plot of $-\ln(P_\infty - P)$ vs. time is nonlinear; in contrast, graphing $(P_\infty - P)^{-1}$ vs. time, as shown in Figure 3, yields a straight line except for the initial few minutes of the reaction. Thus, at these concentrations of CF_3CO_2H, the cleavage is second order in acid and third order overall. The initial deviation from linearity most likely arises from dissolution of CH_4 in CH_2Cl_2 and, possibly, from the higher concentrations of CF_3CO_2H at the start of the reaction.

The reaction of η^5-$C_5H_5Fe(CO)_2C_2H_5$ with CF_3CO_2H shows a kinetic behavior similar to that of the methyl analogue. It is first order in the acid monomer at $[CF_3CO_2H]_a \gtrsim 0.1\ M$, and approaches second order at lower $[CF_3CO_2H]_a$.

The cleavage of η^5-$C_5H_5Fe(CO)_2CH_2Si(CH_3)_3$ by CF_3CO_2H occurs very rapidly in CH_2Cl_2 at 25°C, and acid concentrations higher than 0.1 M could not be employed. As with the methyl and ethyl complexes at these acid concentrations, a plot of $-\ln k_{obs}$ vs. $\ln[CF_3CO_2H]_M$ is nonlinear. Consequently, only a lower limit for the overall second-order rate constant could be obtained. The corresponding reaction of the other complexes η^5-$C_5H_5Fe(CO)_2R$ containing a primary alkyl group, viz. $CH_2CH_2C_6H_5$ and $CH_2C(CH_3)_3$, was studied at $[CF_3CO_2H]_a > 0.1\ M$ and gave linear plots of $-\ln k_{obs}$ vs. time, with slopes near 1.

The benzyl complex, η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$, undergoes cleavage more slowly than the aforementioned alkyl complexes, and higher acid concentra-

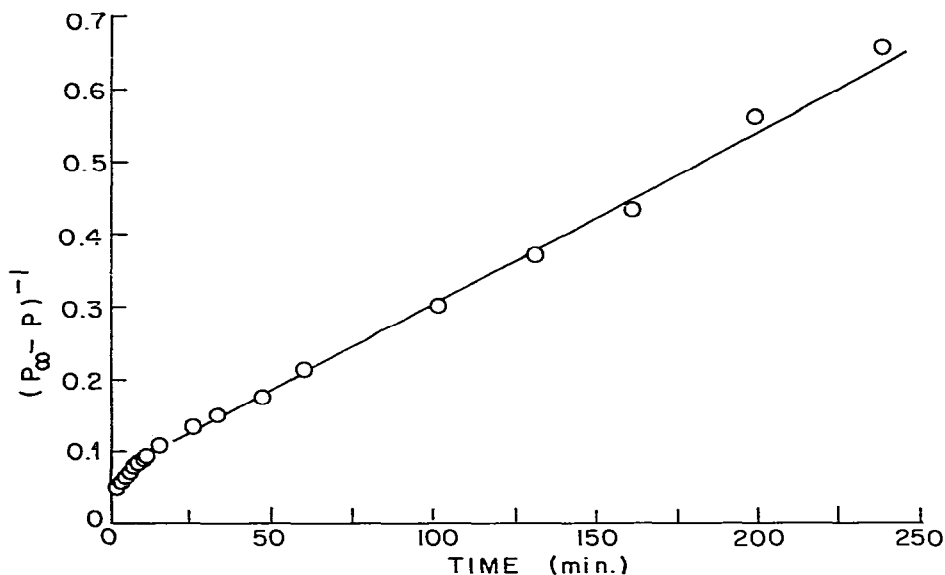Fig. 3. Plot of manometric data for the cleavage of η^5-$C_5H_5Fe(CO)_2CH_3$ (0.86 M) by a tenfold deficiency of CF_3CO_2H in CH_2Cl_2 at 25°C.

tions, 1.3—2.5 M, were necessary to follow the reaction. Possibly because of these higher concentrations, which no doubt alter the nature of the reaction medium, the calculated second-order rate constant, k_2, increases with increasing $[CF_3CO_2H]_a$. A similar behavior was also observed for η^5-$C_5H_5Fe(CO)_2CH$-$(CH_3)C_6H_5$, which was studied in the acid concentration range 0.99—2.56 M. Additionally, the latter complex showed slow decomposition over the relatively long, 1.3—6.0 h reaction times employed. The phenyl complex, η^5-C_5H_5Fe-$(CO)_2C_6H_5$, reacts too rapidly to be studied by the techniques used in this investigation.

Kinetic data for the reaction of the various η^5-$C_5H_5Fe(CO)_2R$ complexes with a tenfold excess of CF_3CO_2H in CH_2Cl_2 at 25°C are presented in Table 1. Second-order rate constants for the cleavage are given in Table 2.

As shown in Table 1, within experimental error, essentially equal rate constants k_{obs} were obtained for the cleavage of η^5-$C_5H_5Fe(CO)_2CH_3$ and η^5-$C_5H_5Fe(CO)_2CD_3$ by excess CF_3CO_2H under comparable concentration conditions in CH_2Cl_2 at 25°C.

The cleavage of η^5-$C_5H_5Fe(CO)_2CH_3$ by CF_3CO_2D in CH_2Cl_2 at 25°C was studied in the acid concentration range 0.18—0.51 M. The rate constant k_{obs} shows a reasonable linear dependence on $[CF_3CO_2D]_M$ *, yielding $k_2 = 2.96 \times 10^{-3} M^{-1} s^{-1}$ (±15%). Comparison with k_2 for the corresponding cleavage by CF_3CO_2H affords an isotope effect, k_{2_H}/k_{2_D} of 4.7.

The influence of solvent on the rate of the reaction between η^5-$C_5H_5(CO)_2CH_3$ and CF_3CO_2H was examined using CH_2ClCH_2Cl and C_6H_6, in addition to CH_2Cl_2. The data are contained in Table 3. At the acid concentrations employed the

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* Calculated by assuming that K_D for CF_3CO_2D is the same as for CF_3CO_2H, i.e., 1.5 M^{-1}.

TABLE 1

KINETIC DATA FOR THE REACTION OF η^5-$C_5H_5Fe(CO)_2R$ WITH A TENFOLD EXCESS OF CF_3CO_2H IN CH_2Cl_2 AT 25.0°C

R	$[CF_3CO_2H]_a$ (M)	k_{obs} (sec^{-1})
CH_3[a]	1.64×10^{-1}	1.65×10^{-3}
	1.46×10^{-1}	1.58×10^{-3}
	1.29×10^{-1}	1.38×10^{-3}
	1.07×10^{-1}	1.13×10^{-3}
CD_3	1.52×10^{-1}	1.99×10^{-3}
	1.35×10^{-1}	1.54×10^{-3}
	1.18×10^{-1}	1.18×10^{-3}
	1.06×10^{-1}	1.04×10^{-3}
C_2H_5	1.80×10^{-1}	6.68×10^{-4}
	1.42×10^{-1}	4.90×10^{-4}
	1.19×10^{-1}	4.47×10^{-4}
	9.87×10^{-2}	3.68×10^{-4}
	7.97×10^{-2}	2.35×10^{-4}
	6.02×10^{-2}	2.18×10^{-4}
	4.96×10^{-2}	1.50×10^{-4}
	4.16×10^{-2}	8.97×10^{-5}
$CH_2Si(CH_3)_3$	9.76×10^{-2}	3.77×10^{-3}
	8.10×10^{-2}	2.80×10^{-3}
	5.93×10^{-2}	1.86×10^{-3}
n-C_4H_9	1.73×10^{-1}	8.18×10^{-4}
$CH_2C(CH_3)_3$	2.39×10^{-1}	4.44×10^{-4}
	2.10×10^{-1}	4.01×10^{-4}
$CH_2CH_2C_6H_5$	3.94×10^{-1}	6.21×10^{-4}
	3.43×10^{-1}	4.99×10^{-4}
	2.93×10^{-1}	4.59×10^{-4}
	2.50×10^{-1}	3.64×10^{-4}
	2.08×10^{-1}	2.81×10^{-4}
$CH_2C_6H_5$	2.47	4.05×10^{-4}
	2.37	3.87×10^{-4}
	2.01	3.06×10^{-4}
	1.53	2.04×10^{-4}
	1.31	1.81×10^{-4}
$CH(CH_3)C_6H_5$	2.56	5.32×10^{-4}
	0.99	1.40×10^{-4}

[a] Additional data are plotted in Figure 2.

cleavage is first order in $[CF_3CO_2H]_M$, calculated from the reported values of K_D in CH_2ClCH_2Cl and C_6H_6 [26] (vide supra), and second order overall. Little variation is seen in k_2 for the three solvents. The above reaction was also examined under synthetic conditions in pentane and in THF at 25°C. The cleavage of 2×10^{-2} M η^5-$C_5H_5Fe(CO)_2CH_3$ with approximately tenfold acid in pentane was virtually complete in ca. 1 h, but formation of an oil prevented kinetic studies from being conducted. Under comparable conditions of concentration, there was no detectable reaction between η^5-$C_5H_5Fe(CO)_2CH_3$ (or η^5-C_5H_5Fe-$(CO)_2CH_2CH_2C_6H_5$) and excess CF_3CO_2H in THF over a period of several hours. This lack of reactivity likely results from an acid—base interaction of CF_3CO_2H with the solvent.

Rate data for the cleavage of η^5-$C_5H_5Fe(CO)_2CH_3$ by CF_3CO_2H in CH_2Cl_2 at

TABLE 2

SECOND-ORDER RATE CONSTANTS FOR THE CLEAVAGE OF η^5-C$_5$H$_5$Fe(CO)$_2$R BY CF$_3$CO$_2$H IN CH$_2$Cl$_2$ AT 25.0°C

R	$k_2(M^{-1}\,sec^{-1})$	Rel. k_2	Taft $\sigma^{*\,a}$	ν(C≡O) (cm^{-1}) [b]
C$_6$H$_5$	v. fast [c]		+0.60	1016, 1959
CH$_2$Si(CH$_3$)$_3$	>4.8 × 10^{-2}	>110	−0.26	2003, 1944
CH$_3$	1.39 × 10^{-2} [d,e]	32	0.00	2005, 1944
n-C$_4$H$_9$	6.49 × 10^{-3} [f]	15	−0.13	2001, 1941
C$_2$H$_5$	4.79 × 10^{-3} [d,e]	11	−0.10	1996, 1941
CH$_2$C(CH$_3$)$_3$	2.75 × 10^{-3} [d]	6.2	−0.16	1999, 1938
CH$_2$CH$_2$C$_6$H$_5$	2.32 × 10^{-3} [d]	5.3	+0.08	2000, 1943
CH(CH$_3$)C$_6$H$_5$	~5.1 × 10^{-4} [g]	~1.2	+0.11	1999, 1942
CH$_2$C$_6$H$_5$	4.4 × 10^{-4} [h]	1.0	+0.22	2004, 1947
CH(CH$_3$)$_2$	v. slow [i]		−0.19	1996, 1935

[a] From ref. 48. [b] In CH$_2$Cl$_2$. [c] $t_{1/2}$ ~ 2.5 min when [CF$_3$CO$_2$H]$_a$, in tenfold excess over the complex, is 3.2 × 10^{-2} M. [d] ±5%. [e] From data on runs with [CF$_3$CO$_2$H]$_a$ ≳0.1 M. [f] Based on only one run. [g] ±35%. [h] ±20%. [i] $t_{1/2}$ ~1 day when [CF$_3$CO$_2$H]$_a$, in tenfold excess over the complex, is 0.23—0.58 M.

25°C in the presence of added salt are summarized in Table 4. Depending on the ionic substance introduced, very small positive or negative salt effects are noted.

The dependence of k_2 on the temperature was determined for the reaction of η^5-C$_5$H$_5$Fe(CO)$_2$CH$_3$ with CF$_3$CO$_2$H in CH$_2$ClCH$_2$Cl at 13.9—25.0°C. The data are incorporated into Table 3. In calculating k_2 at 13.9 and 19.5°C it was assumed that the dimerization constant, K_D, for CF$_3$CO$_2$H remains unchanged at 1.5 M^{-1} over the narrow temperature range employed. The activation parameters for the overall second-order reaction are E_a = 8.1 ± 1.2 kcal/mole, $\Delta H^{\neq}$ = 7.5 ± 1.2 kcal/mole and $\Delta S^{\neq}$ = −41 ± 2 eu.

(B) Cleavage by CHCl$_2$CO$_2$H. Since CHCl$_2$CO$_2$H is a weaker acid than CF$_3$CO$_2$H

TABLE 3

RATE DATA FOR THE REACTION OF η^5-C$_5$H$_5$Fe(CO)$_2$CH$_3$ WITH A TENFOLD EXCESS OF CF$_3$CO$_2$H in CH$_2$ClCH$_2$Cl AND C$_6$H$_6$

Solvent	Temp. (°C)	[CF$_3$CO$_2$H]$_a$ (M)	k_{obs}(sec^{-1})	$k_2(M^{-1}\,sec^{-1})$ [a]
CH$_2$ClCH$_2$Cl	25.0	1.85 × 10^{-1}	2.57 × 10^{-3}	1.92 × 10^{-2}
		1.78 × 10^{-1}	2.43 × 10^{-3}	
		1.70 × 10^{-1}	2.35 × 10^{-3}	
		1.55 × 10^{-1}	1.81 × 10^{-3}	
		1.39 × 10^{-1}	1.60 × 10^{-3}	
CH$_2$ClCH$_2$Cl	19.5	1.94 × 10^{-1}	2.02 × 10^{-3}	1.41 × 10^{-2}
		1.82 × 10^{-1}	1.80 × 10^{-3}	
		1.68 × 10^{-1}	1.78 × 10^{-3}	
		1.59 × 10^{-1}	1.59 × 10^{-3}	
		1.40 × 10^{-1}	1.22 × 10^{-3}	
CH$_2$ClCH$_2$Cl	13.9	2.86 × 10^{-1}	1.98 × 10^{-3}	1.14 × 10^{-2}
		2.23 × 10^{-1}	1.75 × 10^{-3}	
		2.02 × 10^{-1}	1.71 × 10^{-3}	
		1.69 × 10^{-1}	9.66 × 10^{-4}	
C$_6$H$_6$	25.0	2.47 × 10^{-1}	2.26 × 10^{-3}	1.58 × 10^{-2}
		2.30 × 10^{-1}	2.16 × 10^{-3}	

[a] Average value, generally calculated by using the data obtained at 3 or 4 highest [CF$_3$CO$_2$H]$_a$.

TABLE 4

RATE DATA FOR THE REACTION OF η^5-$C_5H_5Fe(CO)_2CH_3$ WITH A TENFOLD EXCESS OF CF_3CO_2H IN THE PRESENCE OF ADDED SALT IN CH_2Cl_2 AT 25.0°C

Salt, conc. (M)		$[CF_3CO_2H]_a$ (M)	$k_{obs}(sec^{-1})$	$k_{obs}(sec^{-1})$ without added salt [a]
$[(C_2H_5)_4N]Cl$,	9.41×10^{-3}	1.21×10^{-1}	1.16×10^{-3}	1.29×10^{-3}
	9.39×10^{-3}	1.49×10^{-1}	1.06×10^{-3}	1.58×10^{-3}
$[(n\text{-}C_4H_9)_4N]I$ [b],	9.74×10^{-3}	1.66×10^{-1}	1.51×10^{-3}	1.76×10^{-3}
$[(n\text{-}C_4H_9)_4N]O_2CCH_3$,	1.16×10^{-2}	1.65×10^{-1}	1.39×10^{-3}	1.75×10^{-3}
$[(C_2H_5)_4N]O_2CCF_3$,	9.41×10^{-3}	1.47×10^{-1}	1.90×10^{-3}	1.55×10^{-3}
	9.50×10^{-3}	1.78×10^{-1}	2.32×10^{-3}	1.89×10^{-3}

[a] Calculated by using $k_2 = 1.39 \times 10^{-2} M^{-1} sec^{-1}$ (Table 2). [b] η^5-$C_5H_5Fe(CO)_2I$ formed in the reaction.

($K_a = 4.3 \times 10^{-2}$ and $5.88 \times 10^{-1} M$, respectively, in H_2O at 25°C [28]), it was used to examine the cleavage of the aryl complexes η^5-$C_5H_5Fe(CO)_2R$, which react too rapidly with CF_3CO_2H to be followed by the techniques employed here. Exploratory kinetic runs revealed that the reaction according to equation 1

TABLE 5

RATE DATA FOR THE REACTION OF THE ARYL COMPLEXES η^5-$C_5H_5Fe(CO)_2R$ WITH A TENFOLD EXCESS OF $CHCl_2CO_2H$ AT 25.0°C

R	Solvent	$[CHCl_2CO_2H]_a$ (M)	$k_{obs}(sec^{-1})$
C_6H_5	CH_2Cl_2	1.67×10^{-1}	1.22×10^{-3}
		1.30×10^{-1}	8.50×10^{-4}
		1.01×10^{-1}	7.41×10^{-4}
		8.90×10^{-2}	6.15×10^{-4}
		8.00×10^{-2}	5.73×10^{-4}
		7.92×10^{-2}	4.68×10^{-4}
		6.04×10^{-2}	3.28×10^{-4}
		4.08×10^{-2}	1.87×10^{-4}
C_6H_5	CH_2ClCH_2Cl	1.67×10^{-1}	1.18×10^{-3}
		1.48×10^{-1}	9.71×10^{-4}
		1.16×10^{-1}	7.03×10^{-4}
C_6H_5	C_6H_6	1.74×10^{-1}	8.38×10^{-4}
		1.51×10^{-1}	5.76×10^{-4}
$p\text{-}C_6H_4Cl$	CH_2Cl_2	1.82×10^{-1}	3.51×10^{-4}
		1.52×10^{-1}	2.99×10^{-4}
		1.27×10^{-1}	2.21×10^{-4}
		1.02×10^{-1}	1.88×10^{-4}
		7.67×10^{-2}	1.18×10^{-4}
		6.03×10^{-2}	1.02×10^{-4}
$p\text{-}C_6H_4F$	CH_2Cl_2	1.66×10^{-1}	1.28×10^{-3}
		1.40×10^{-1}	1.71×10^{-3}
		1.23×10^{-1}	1.49×10^{-3}
		9.66×10^{-2}	9.63×10^{-4}
		8.04×10^{-2}	8.43×10^{-4}
		6.07×10^{-2}	5.58×10^{-4}
		4.13×10^{-2}	3.73×10^{-4}
$p\text{-}C_6H_4CH_3$	CH_2Cl_2	6.90×10^{-2}	3.87×10^{-3}
		5.28×10^{-2}	2.20×10^{-3}
		4.38×10^{-2}	1.86×10^{-3}
		4.34×10^{-2}	1.53×10^{-3}
		3.02×10^{-2}	9.77×10^{-4}

of a given η^5-$C_5H_5Fe(CO)_2R$ is indeed much slower with $CHCl_2CO_2H$ than with CF_3CO_2H. Thus, with 0.16 M acid in a tenfold excess over η^5-$C_5H_5Fe(CO)_2CH_3$ in CH_2Cl_2 at 25°C, the cleavage by $CHCl_2CO_2H$ has a $t_{1/2}$ of ca. 24 h whereas that by CF_3CO_2H is 50% complete in ca. 7 min. Similarly, under the above conditions with 3.2×10^{-2} M acid, the reactions of η^5-$C_5H_5Fe(CO)_2C_6H_5$ with $CHCl_2CO_2H$ and CF_3CO_2H have half-lives of 16 and <2.5 min, respectively.

Rate data obtained by infrared spectroscopy for the cleavage of the aryl complexes by excess $CHCl_2CO_2H$ are presented in Table 5. Good linear plots resulted on graphing $-\ln(A - A_\infty)$ vs. time, showing that the reaction is first order in η^5-$C_5H_5Fe(CO)_2R$. Unfortunately, the dimerization constant, K_D, for $CHCl_2CO_2H$ is known only in C_6H_6 ($K_D = 27.1 \pm 1.9$ M^{-1} at 25°C [29]) of the three solvents employed in this work. Thus it was not possible to determine $[CHCl_2CO_2H]_M$ and the order of the reaction in acid.

This notwithstanding, inspection of the data in Table 5 reveals that the observed rate constant, k_{obs}, in equation 2 increases as the σ^+ value [30] for the para substituent on the phenyl ring (enclosed in parentheses) becomes more negative, i.e., p-C_6H_4Cl (0.11) < C_6H_5 (0.00) < p-C_6H_4F (−0.07) < p-$C_6H_4CH_3$ (−0.31). This order is typical of electrophilic substitution and cleavage reactions. Although ρ cannot be calculated as accurately as desirable from these data, it appears to be approximately −5.4.

The cleavage of η^5-$C_5H_5Fe(CO)_2C_6H_5$ by $CHCl_2CO_2H$ at 25°C was also studied in CH_2ClCH_2Cl and C_6H_6. The appropriate rate data are given in Table 5. A comparison of the values of k_{obs} obtained at comparable concentrations of the acid reveals that the reaction is somewhat faster in CH_2Cl_2 and CH_2ClCH_2Cl than in C_6H_6.

Discussion

The observed first- and second-order dependence of the reaction of η^5-C_5H_5Fe-$(CO)_2CH_3$ with CF_3CO_2H on the monomer acid concentration, at high ($\gtrsim 0.1$ M) and low $[CF_3CO_2H]_a$, respectively, may be explained by the scheme in equation 7.

$$\eta^5\text{-}C_5H_5Fe(CO)_2CH_3 + CF_3CO_2H \underset{k'}{\overset{k}{\rightleftharpoons}} \eta^5\text{-}C_5H_5Fe(CO)_2CH_3 \cdot CF_3CO_2H$$

$$k'' \downarrow CF_3CO_2H$$

$$\eta^5\text{-}C_5H_5Fe(CO)_2OC(O)CF_3 + CH_4 + CF_3CO_2H$$

$$(7)$$

By assuming a steady-state concentration of the adduct η^5-$C_5H_5Fe(CO)_2CH_3 \cdot CF_3CO_2H$, the rate expression in equation 8 is derived.

$$-\frac{d[\eta^5\text{-}C_5H_5Fe(CO)_2CH_3]}{dt} = \frac{kk''[\eta^5\text{-}C_5H_5Fe(CO)_2CH_3][CF_3CO_2H]_M^2}{k' + k''[CF_3CO_2H]_M} \tag{8}$$

An examination of this rate law at the extremes of the acid concentration leads to the following limiting rate expressions. At high $[CF_3CO_2H]_M$,

$k''[CF_3CO_2H]_M \gg k'$, and hence

$$-\frac{d[\eta^5\text{-}C_5H_5Fe(CO)_2CH_3]}{dt} = k[\eta^5\text{-}C_5H_5Fe(CO)_2CH_3][CF_3CO_2H]_M \qquad (9)$$

At low $[CF_3CO_2H]_M$, $k' \gg k''[CF_3CO_2H]_M$, leading to

$$-\frac{d[\eta^5\text{-}C_5H_5Fe(CO)_2CH_3]}{dt} = \frac{kk''}{k'}[\eta^5\text{-}C_5H_5Fe(CO)_2CH_3][CF_3CO_2H]_M^2 \qquad (10)$$

A crucial test of the validity of the mechanism in equation 7 is based on a graphical representation of the equation

$$k_{obs} = \frac{kk''[CF_3CO_2H]_M^2}{k' + k''[CF_3CO_2H]_M} \qquad (11)$$

which combines equations 2 (R = CH_3) and 8. This equation may also be written in the form

$$\frac{[CF_3CO_2H]_M}{k_{obs}} = \frac{1}{k} + \frac{k'}{kk''[CF_3CO_2H]_M} \qquad (12)$$

Hence a plot of $\dfrac{[CF_3CO_2H]_M}{k_{obs}}$ vs. $\dfrac{1}{[CF_3CO_2H]_M}$ should yield a straight line whose slope and intercept are equal to k'/kk'' and $1/k$, respectively.

Figure 4 shows such a plot. The value of k derived therefrom is 1.9×10^{-2} M^{-1} sec^{-1}, and may be compared with a rate constant of 1.39×10^{-2} M^{-1} sec^{-1} obtained from the plot in Figure 2 (Table 2). The agreement is fair if one takes into account some scatter of the data points in Figures 2 and 4. By using $k = 1.9 \times 10^{-2}$ M^{-1} sec^{-1} in conjunction with the slope of the line in Figure 4, the ratio k'/k'' comes out to be 4.9×10^{-2} M.

A sequence of reactions similar to that in equation 7 may be invoked to account for the observed kinetic behavior toward CF_3CO_2H of the complexes $\eta^5\text{-}C_5H_5Fe(CO)_2C_2H_5$ and $\eta^5\text{-}C_5H_5Fe(CO)_2CH_2Si(CH_3)_3$, studied in less detail than the methyl analogue. The cleavage of the other alkyl complexes was examined only at the higher acid concentrations ($\gtrsim 0.1$ M) and accordingly exhibited first-order dependence on $[CF_3CO_2H]_M$. In the absence of any evidence to the contrary, we assume that the alkyl complexes $\eta^5\text{-}C_5H_5Fe(CO)_2R$ react uniformly as shown in equation 7 for $\eta^5\text{-}C_5H_5Fe(CO)_2CH_3$.

The second-order rate constants, k_2, listed in Table 2 for the cleavage of the various alkyl complexes $\eta^5\text{-}C_5H_5Fe(CO)_2R$, are also those designated as k in equation 9. They refer to the bimolecular interaction between $\eta^5\text{-}C_5H_5Fe(CO)_2R$ and CF_3CO_2H given as part of equation 7.

These data show that the reactivity of CF_3CO_2H toward $\eta^5\text{-}C_5H_5Fe(CO)_2R$ follows the order R = $C_6H_5 > CH_2Si(CH_3)_3$ (>110) $> CH_3$ (32) $>$ n-C_4H_9 (15) $>$ C_2H_5 (11) $> CH_2C(CH_3)_3$ (6.2) $> CH_2CH_2C_6H_5$ (5.3) $> CH(CH_3)C_6H_5$ (~ 1.2) $\gtrsim$ $CH_2C_6H_5$ (1.0) $> CH(CH_3)_2$, the relative values of the rate constant being enclosed in parentheses. In general, when R is an alkyl group, the range of the relative reactivity is not wide. Moreover, both electronic factors, e.g., R = CH_2Si-$(CH_3)_3 > CH_3$ or $CH_2C(CH_3)_3$, and steric factors, e.g., $CH_3 > CH(CH_3)_2$ or CH_2C-$(CH_3)_3$, as well as $trans$-4-$C_6H_{10}CH_3 > cis$-4-$C_6H_{10}CH_3$, obtained by Rogers and
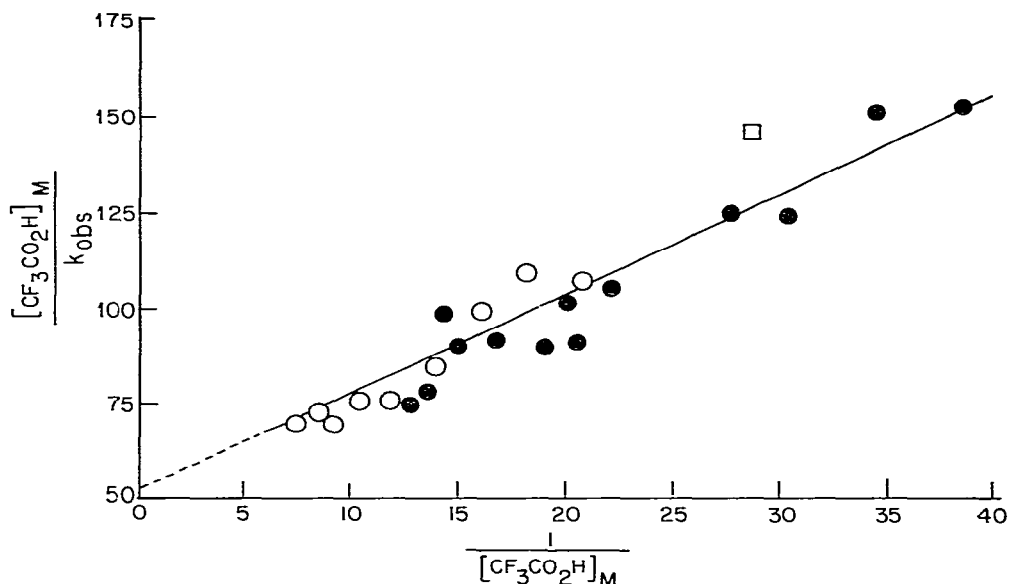
Fig. 4. Cleavage of η^5-$C_5H_5Fe(CO)_2CH_3$ by a tenfold excess of CF_3CO_2H in CH_2Cl_2 at 25°C. The data are those used in Figure 2.

Baird [12], appear to influence the propensity of η^5-$C_5H_5Fe(CO)_2R$ to undergo cleavage. Except when R = C_6H_5, the foregoing pattern parallels the order of reactivity toward η^5-$C_5H_5Fe(CO)_2R$ of $HgCl_2$, where direct interaction between iron and mercury has been proposed [5]. However, it differs noticeably from the rate profile for the reaction of η^5-$C_5H_5Fe(CO)_2R$ with SO_2, which is thought to involve backside interaction of SO_2 with R [1,2]. Thus it would appear that the acid cleavage of the alkyl complexes proceeds by an electrophilic attack of CF_3CO_2H at the metal.

Central to any discussion of mechanistic details of the cleavage process in equation 7 (for R = alkyl in general) is the nature of the proposed 1/1 adduct. A reasonable structure of this intermediate, I, along with a sequence of steps thought to comprise the scission reaction, is depicted in Scheme 1.

Intermediate I may be regarded as a low-concentration species in which hydrogen has not been transferred completely from the acid to the metal, but instead bridges the two moieties. Stable hydrogen-bridged structures are known in organo-transition metal chemistry, and include those with metal—hydrogen—silicon bonds [31] and metal—hydrogen—metal bonds in general [32]. Moreover, such structures are amply precedented in the behavior of carboxylic acids toward bases [33]. For example, carboxylic acids readily hydrogen-bond to the amines with varying degrees of proton transfer depending on the strength of the acid and the base [34,35]. An alternative structural assignment to the initial 1/1 adduct, that of a tight ion pair similar to III in Scheme 1, seems unlikely. This is because the rate of the cleavage reaction of the methyl complex is virtually unaffected by the nature of the solvent, and changes little on addition of a salt. Unless the presence of ca. 0.2 M CF_3CO_2H exerts a leveling effect on the reaction medium for CH_2Cl_2, CH_2ClCH_2Cl and C_6H_6, these results would

SCHEME 1
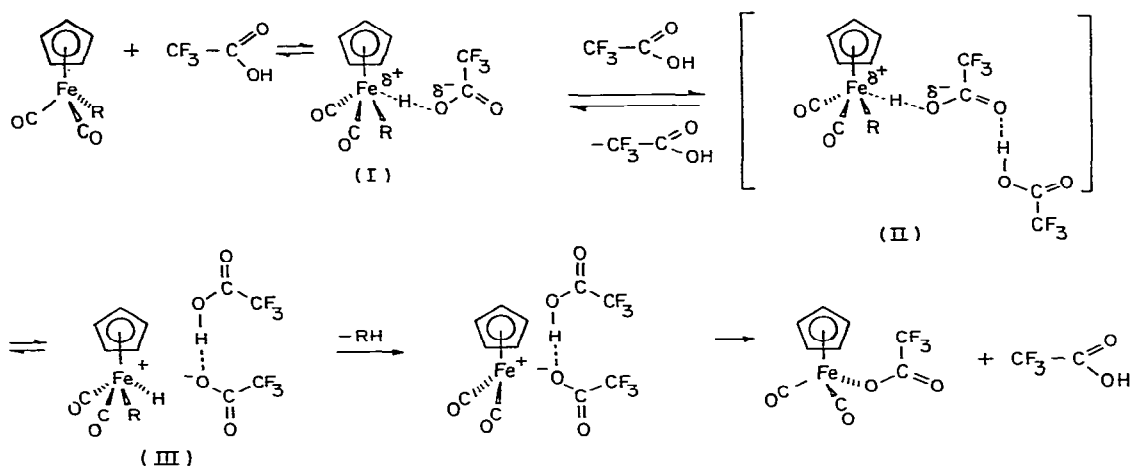
seem to rule out any substantial increase in the separation of charge during the formation of the intermediate η^5-$C_5H_5Fe(CO)_2R \cdot CF_3CO_2H$ (k-step, equation 7). The observed isotope effect, $k_H/k_D = 4.7$, for the cleavage of η^5-C_5H_5Fe-$(CO)_2CH_3$ with CF_3CO_2H and CF_3CO_2D indicates a considerable degree of bond breaking of the O—H and O—D in the transition state for the first step of the cleavage, and appears to be in accord with the proposed structure of I. Likewise, the large negative value of $\Delta S^{\neq}$ and the relatively small value of $\Delta H^{\neq}$ are consistent with the suggested bimolecular interaction between η^5-$C_5H_5Fe(CO)_2R$ and CF_3CO_2H.

The role of a second molecule of CF_3CO_2H in the cleavage is not fully understood. However, a reasonable postulate would be that this molecule assists in the dissociation of the hydrogen bridge in I to furnish III by stabilizing the incipient acetate anion through hydrogen-bonding as shown in II. Carboxylic acids commonly engage in hydrogen-bonding with polar substances, including $CHCl_3$ and CH_2Cl_2 [33]. Since it is not possible to determine the value of k'' (equation 7) for the different alkyl complexes from the data on hand, little else can be said about this step of the reaction. It may be added, however, that second-order dependence on the concentration of the organic reactant has been observed for the amines interacting with cationic manganese and rhenium carbonyls [36], (methoxycarbene)pentacarbonylchromium [37] or organic esters [38]. As in this study, it has been ascribed to hydrogen-bonding. Completing the cleavage in Scheme 1 is reductive elimination of RH from III followed by coordination of the acetate anion to iron to afford the isolable product, η^5-C_5H_5Fe-$(CO)_2OC(O)CF_3$.

An attempt was made at detection of species III when investigating the complex with R = $C(CH_3)_3$. It was thought that this tertiary alkyl group would not readily engage in reductive elimination with hydrogen to give $CH(CH_3)_3$, thus conferring some stability on III. Although the infrared spectrum of a solution containing η^5-$C_5H_5Fe(CO)_2C(CH_3)_3$ and CF_3CO_2H showed two $\nu(C\equiv O)$ bands in the region expected for a cationic η^5-$C_5H_5Fe(CO)_2(R)H^+$, further efforts at characterization of this species proved unsuccessful.

The reaction of η^5-$C_5H_5Fe(CO)_2CH_2C_2H_5$ with CF_3CO_2D according to equation 1 is accompanied by the deuteriation of the phenyl ring. The latter process, which proceeds more rapidly than the cleavage, has been reported independently by Setkina [39,40] for both η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$ and η^5-$C_5H_5Fe(CO)_2CH$-$(CH_3)C_6H_5$. Since the mechanism of the deuterium exchange and the cleavage in the system η^5-$C_5H_5Fe(CO)_2CH_2C_6H_5$—CF_3CO_2D is presently under examination by Johnson [41], no detailed investigation was conducted in this laboratory.

The mechanism in Scheme 1 is in full accord with the recently reported stereochemical outcome at iron and at α carbon for the acid cleavage of the optically active η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ (R = CH_3 and C_2H_5) [7] and of η^5-$C_5H_5Fe(CO)_2(cis$- and $trans$-4-$C_6H_{10}CH_3$) [12], respectively. In the first study, partial racemization of unreacted η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]R$ may result from a fluxional behavior of an intermediate analogous to I (or III or both). The depicted pathway would also allow for the observed partial loss of stereochemistry at metal in the formation of η^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]OC(O)CF_3$. In the second study, retention of configuration at the α-carbon atom of 4-$C_6H_{10}CH_3$ may be rationalized by reductive coupling of the cycloalkyl group and deuterium (from CF_3CO_2D) to eliminate 4-$C_6H_{10}DCH_3$.

Mechanisms involving protonation at the metal center have been proposed for the cleavage of transition metal—carbon σ bonds by HCl in coordinatively unsaturated square-planar platinum(II) alkyls and aryls [42—44] and in dialkyl-aurates(I) [45]. Although protonation of the metal is a common behavior of low-valent coordinatively saturated transition metal complexes [32,46], such a pathway for the scission of metal—alkyl bonds had not been fully documented prior to the present mechanistic study.

By way of contrast, the aryl complexes η^5-$C_5H_5Fe(CO)_2R$ appear to react with acetic acids via a mechanism different from that proposed for the alkyl complexes based on the following observations. First, as shown in Table 2, the cleavage of η^5-$C_5H_5Fe(CO)_2C_6H_5$ by CF_3CO_2H is much faster than that of any alkyl complex investigated here. Moreover, the order η^5-$C_5H_5Fe(CO)_2C_6H_5 >$ η^5-$C_5H_5Fe(CO)_2CH_3$ holds for the reaction with $CHCl_2CO_2H$. The reactivity pattern, R = aryl > alkyl, was previously noted for the acid cleavage of HgR_2 [47] and has been ascribed to proton attack at the α carbon of the phenyl ring. Second, the approximate ρ value of -5.4 for the scission of the aryls η^5-C_5H_5Fe-$(CO)_2R$ by $CHCl_2CO_2H$ indicates a considerable sensitivity of the reaction to substituent effects. It may be compared with $\rho = -4.3$ and -1.2 for the SO_2
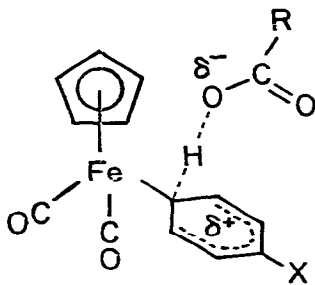
(IV)

insertion [1] and the $HgCl_2$ cleavage [5], respectively, of the same η^5-C_5H_5Fe-$(CO)_2R$ aryl complexes. These reactions were proposed to proceed by electrophilic attack of SO_2 at the phenyl ring and of $HgCl_2$ at the metal. A comparison of the three ρ values would seem to suggest that the acetic acids interact with the α-carbon atom as shown in IV. Unfortunately, further details of the mechanism could not be elucidated because of lack of data on the nature of $CHCl_2CO_2H$ in the chlorinated hydrocarbons used in this work.

Acknowledgement

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