THE CHROMIC ACID OXIDATION OF ARYL TRIFLUOROMETHYL ALCOHOLS: ISOTOPE AND SUBSTITUENT EFFECTS[1]

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ABSTRACT

The mechanism of the chromic acid oxidation of eight aryltrifluoromethylcarbinols has been studied in acetic acid solution. Electron-donating substituents accelerate the reaction and a good correlation of rate with σ^+ values has been found. The rho value is -1.01. Deuterium isotope effects for the oxidation of five of these compounds have been determined and the magnitude of the isotope effect has been found to correlate inversely with the ease of oxidation of the alcohol.

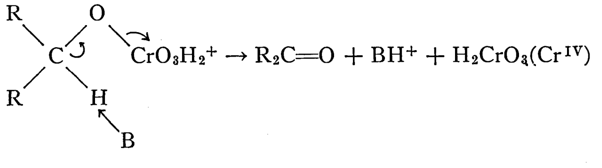
The results are interpreted in terms of a unimolecular decomposition of the chromate ester of the alcohol.

Previous work in this laboratory showed that unusually large kinetic isotope effects were observed when a group of aryl trifluoromethyl alcohols ($ArCDOHCF_3$) were oxidized to ketones by alkaline permanganate (1, 2). The values of k_H/k_D of 16:1 found at 25° are more than double those expected for complete loss of the C—H (D) stretching mode in the transition state (3, 4). Since proton tunnelling did not seem to be the dominant factor in these and related reactions the anomalous isotope effects have been tentatively attributed to alterations in the C—H bending modes in the transition state. It was of interest, then, to determine if the unusual isotope effects observed in the permanganate oxidation also occur in the oxidation of these alcohols by chromic acid. A "normal" isotope effect of 6.6 at 25° was found for the chromic acid oxidation of isopropyl-*d* alcohol, $(CH_3)_2CDOH$ (5).

A great deal of work has been done in elucidating the mechanism of chromic acid oxidation of alcohols, particularly by Westheimer (5–10), Roček (11, 12), and Kwart (13–15) and their colleagues.

The work of Westheimer and his group on the oxidation of isopropyl alcohol can be summarized as follows: (*a*) the reaction is acid catalyzed with the rate being proportional to the first (or in some cases a higher) power of the hydrogen ion concentration (or h_0), (*b*) the reaction is much faster in acetic acid solution than in mineral acids of the same H_0 value, (*c*) the transition state is a monochromium, not a dichromium, species, (*d*) the C—H bond at the carbinol carbon is broken in the rate-controlling step. Chromate esters of alcohols are known to exist under the reaction conditions and the following mechanism, in which such an ester decomposes by proton loss to any available base (probably a water molecule), was put forward.

$$R_2CHOH + HCrO_4^- + 2H^+ \rightleftharpoons R_2CHOCrO_3H_2^+ + H_2O$$



$$R_2C(H\cdots B)\text{—}O\text{—}CrO_3H_2^+ \rightarrow R_2C{=}O + BH^+ + H_2CrO_3(Cr^{IV})$$

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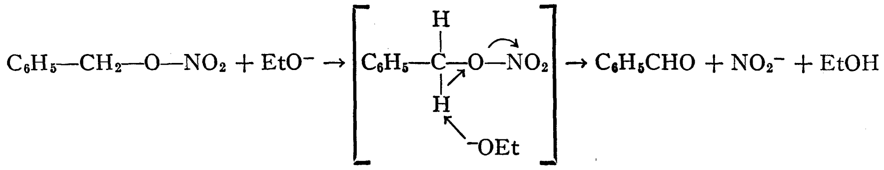
Some elegant work on the induced oxidation of added substrates has traced the fate of the chromium (IV) intermediate formed in such reactions and which is eventually converted to chromium (III) (16, 17).

It has not proved possible to detect the participation of base in the rate-controlling step of the oxidation and this has led to other mechanisms being suggested. Furthermore, the Hammett reaction constant, rho, for the chromic acid oxidation of arylmethylcarbinols has a value of -1.01 (13) and this is not very easily reconciled with a rate-controlling proton abstraction from the α-carbon of the ester, even when the pre-equilibrium step is considered.

The effect of substituents on such a reaction has been elegantly illustrated by Buncel and Bourns (18) in their work on the decomposition of benzyl nitrate by ethoxide ions.



$$C_6H_5\text{—}CH_2\text{—}O\text{—}NO_2 + EtO^- \rightarrow \left[C_6H_5\text{—}\overset{H}{\underset{\underset{^-OEt}{H}}{C}}\text{—}O\text{—}NO_2 \right] \rightarrow C_6H_5CHO + NO_2^- + EtOH$$

This reaction shows a deuterium isotope effect of 5.04 at 60° and a ^{15}N isotope effect of 1.0196 at 30° indicating that the carbon–hydrogen and the nitrogen–oxygen bonds are broken simultaneously in the course of the reaction. In this case it is evident that the hydrogen is being abstracted as a proton and the large positive rho value of $+3.40$ shows that the effect of substituents on the cleavage of the α-carbon–hydrogen bond is greater than on the more remote oxygen–nitrogen bond.

In subsequent papers in this series evidence will be presented in support of the idea that the chromate ester is a reactive intermediate which decomposes unimolecularly to products.

$$R_2CHOCrO_3H_2^+ \rightarrow R_2C{=}O + H_3CrO_3^+$$

The results presented herein are in accord with such a mechanism although they do not uniquely require it.

A unimolecular decomposition of the ester by an internal proton transfer has been previously suggested by Kwart and Francis (14) and the possibility of an internal hydride transfer has been noted by Littler (19). The relative merits of the cyclic and acyclic mechanisms have been discussed by Roček, Westheimer, Eschenmoser, Moldovanyi, and Schreiber (20) and by Stewart (21).

RESULTS AND DISCUSSION

The rates of oxidation of eight aryltrifluoromethylcarbinols have been determined at 25° in a 77.2% acetic acid solution containing 3.20 M perchloric acid. The deuterium isotope effects for five of these alcohols were also determined. The results are presented in Table I. A Hammett plot for both the protio and deuterio compounds is shown in Fig. 1. The σ^+ values were used since they gave a somewhat better correlation with the measured rate constants.

Attempts were made to determine the rates of oxidation of p-methoxyphenyltrifluoromethylcarbinol and β-naphthyltrifluoromethylcarbinol. Since the difference between σ and σ^+ values for the p-methoxy and the α-naphthyl group are greater than for any of the other groups they are most useful in differentiating between reactions which follow σ^+

TABLE I

Oxidation of fluoro alcohols in 77.2% acetic acid, 3.20 M $HClO_4$ (H_0 = −2.82), T = 25° C, [Cr^{VI}] = 1.79×10^{-3} M

Alcohol	alc. ($M\times10^3$)	k_2 (l.moles^{-1} sec^{-1})	k_H/k_D
p-t-Butylphenyltrifluoromethylcarbinol	2.68	0.574	
	2.68	0.544	
p-Tolyltrifluoromethylcarbinol	2.68	0.534	
	2.68	0.537	
	2.68	0.564	
	2.68	0.540	
p-Tolyltrifluoromethylcarbinol-α-*d*	2.68	0.0727	7.40±0.20
	2.68	0.0740	
	2.68	0.0747	
	2.68	0.0706	
m-Tolyltrifluoromethylcarbinol	2.68	0.350	
	2.68	0.340	
Phenyltrifluoromethylcarbinol	2.68	0.259	
	2.68	0.250	
	15.3	0.258	
Phenyltrifluoromethylcarbinol-α-*d*	16.1	0.0310	8.53±0.15
	2.68	0.0294	
	2.68	0.0297	
p-Chlorophenyltrifluoromethylcarbinol	2.68	0.174	
	2.68	0.174	
m-Bromophenyltrifluoromethylcarbinol	2.68	0.119	
	2.68	0.106	
	2.68	0.110	
	2.68	0.109	
m-Bromophenyltrifluoromethylcarbinol-α-*d*	2.68	0.0117	9.80±0.20
	2.68	0.0111	
	20.8	0.0113	
m-Nitrophenyltrifluoromethyl carbinol	2.68	0.0494	
	2.68	0.0514	
	2.68	0.0484	
	14.06	0.0453	
	17.22	0.0444	
	15.96	0.0474	
m-Nitrophenyltrifluoromethylcarbinol-α-*d*	17.28	0.00360	12.20±.020
	18.69	0.00367	
3,5-Dinitrophenyltrifluoromethylcarbinol	17.65	0.0116	
	12.81	0.0118	
3,5-Dinitrophenyltrifluoromethylcarbinol-α-*d*	55.10	0.00100	12.93±0.78
	10.92	0.000834	

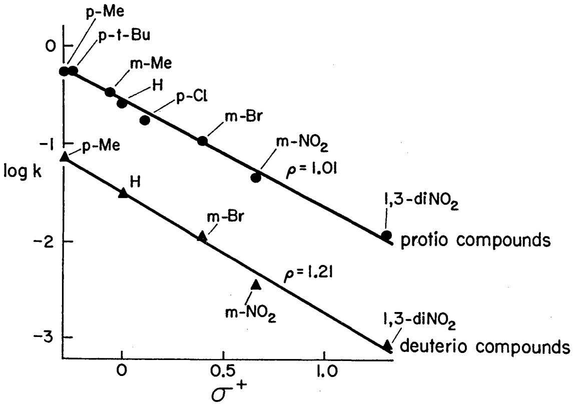


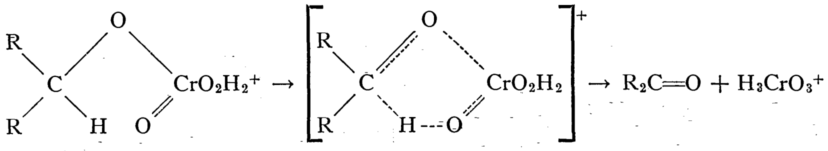
FIG. 1. A Hammett plot for the chromic acid oxidation of $ArCHOHCF_3$ and $ArCDOHCF_3$ in 77.2% acetic acid – 3.20 M perchloric acid.

values and those which follow σ values. Unfortunately both of these alcohols reduced chromium (VI) at a very fast rate in the medium used. This can be attributed to the oxidation of these compounds at sites other than the hydroxylated carbon since it was later found that both anisole and naphthalene were very rapidly oxidized under these conditions.

A rho value of -1.01 was calculated from the slope of the plot in Fig. 1. While other interpretations (6, 13) have been suggested for the negative rho values observed in the oxidation of alcohols by chromic acid the most direct explanation for any reaction exhibiting a negative ρ^+ value is that considerable positive charge is located on the α-carbon atom in the transition state. Further, the observation of very pronounced isotope effects demands that any proposed mechanism include as a rate-determining step, fission of the α-carbon–hydrogen bond.

The oxygen–hydrogen bond of the alcohol is probably not intact in the transition state (ethers are relatively inert to chromium (VI) (6)) nor being broken in the transition state (because of the positive solvent isotope effect observed in this reaction (6)). Westheimer's conclusion, then, that the chromate ester is a reactive intermediate in the oxidation, seems reasonable. The recent study by Roček, Westheimer, Eschenmoser, Moldovanyi, and Schreiber (20) of the chromic oxidation of a hindered alcohol lends further support to the ester being an intermediate in the oxidation. They found that the substrate isotope effect for the hindered alcohol vanished in concentrated acid, i.e. ester formation became rate controlling.

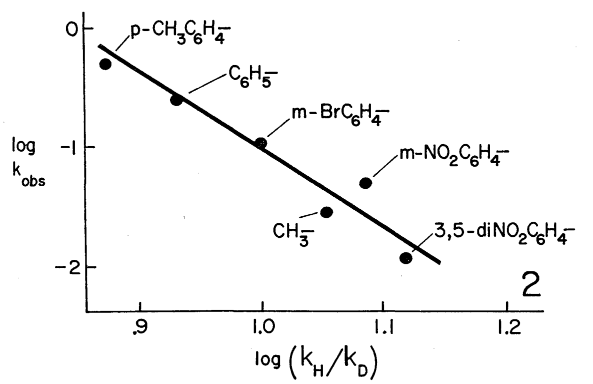
A unimolecular decomposition of the ester can be written in which the hydrogen is bonded in the transition state to both the alcoholic carbon atom and the oxygen atom attached to chromium.



Kwart and Francis have written a similar transition state with the hydrogen being transferred as a proton (14). The question of electron flow in a cyclic transition state such as the above is a vexing one (22, 23) and we prefer to consider the conversion of ester to transition state in the following terms.

The transfer of electrons toward the chromium occurs by formation of carbon–hydrogen–oxygen bonds in the transition state as well as carbon–oxygen–chromium bonds, i.e. partly occupied orbitals are used to bind the transferred hydrogen to both carbon and oxygen in the transition state. The developing carbonyl group in the electron-deficient transition state will be stabilized by electron-donating substituents and this presumably accounts for the negative rho value. (See however Ref. 15.) Protonation of the chromate portion of the ester also increases the reaction rate. The conversion of ester to transition state is thus aided by the combined polarizing effects of an electron-donating aromatic ring and an electron-withdrawing metal cation.

An approximately linear relationship exists between the rates of oxidation of trifluoromethylcarbinols and the observed isotope effects. This relationship, which is illustrated in Fig. 2, fits in well with the suggestion, first made by Wiberg (3), that there should be a general correlation between rates and isotope effects within a group of analogous reactions, slow rates being accompanied by large isotope effects. Wiberg based his predictions on the



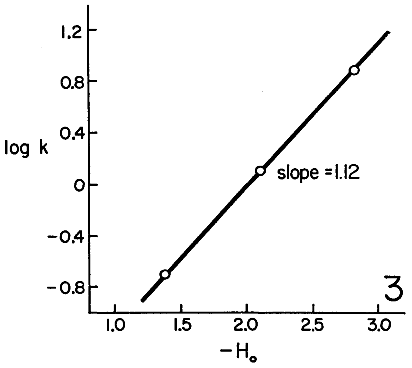


FIG. 2. The variation of isotope effect with rate constant for the chromic acid oxidation of ArCHOHCF$_3$.

FIG. 3. Variation of rate with acidity for the oxidation of phenyltrifluoromethylcarbinol in 77.2% acetic acid.

experimental observation that the isotope effects in the side-chain halogenation of para-substituted toluenes varied from 3.22 to 5.11 at 77°. Since the largest of these isotope effects is somewhat smaller than the maximum effect predicted from a consideration of zero-point energies of the carbon–hydrogen and carbon–deuterium bonds, the variation with rate was explained in terms of factors which could be related to C—H stretching frequencies (3, 24, 25).

In the present case, however, even the smallest isotope effect observed is larger than the maximal effect predicted from a consideration of carbon–hydrogen stretching frequencies. While it is not clear from the present results whether the large isotope effects are due to loss of bending frequencies in the transition state or to a tunnel effect it is interesting to note that a correlation between rate and isotope effect still exists. Such a correlation was not observed by Stewart and Van der Linden (1, 2) in the permanganate oxidation of these alcohols since the rho value for that reaction was almost zero. It does appear, however, that large isotope effects are intimately connected with the trifluoromethyl group or at least with the presence of strongly electron-withdrawing groups adjacent to the site of oxidation. (It should be pointed out here that in the chromic acid oxidation of fluorinated *aliphatic* alcohols a similar situation exists, i.e. the slower the oxidation rate (the more highly fluorinated the alcohol) the higher the isotope effect, with an important exception. 1,1,1,3,3,3-Hexafluoro-2-propanol is oxidized very slowly but its 2-deuterio derivative does not appear to show an anomalously large isotope effect (26).)

The rate of oxidation of phenyltrifluoromethylcarbinol was determined at three different acidities and was found to be linear with h_0 as indicated by the plot in Fig. 3. The acidity data reported in Table II were obtained by a comparative method using *p*-nitrodiphenylamine and 4-chloro-2-nitroaniline as indicators. (The pK_a's of these indicators were assumed to be -2.48 and -1.03 respectively (27).) This observed linearity with h_0, although based on three points only, is in accord with the rate law observed for the oxidation of isopropyl alcohol (9) and benzaldehyde (28) in acetic acid.

$$v = k[\mathrm{R_2CHOH}][\mathrm{HCrO_4^-}]h_0$$

The rho value observed for the oxidation of the aryltrifluoromethylcarbinols is also identical with the value observed for the corresponding oxidation of arylmethylcarbinols in acetic acid (13) and it is probable that they are oxidized via the same reaction path.

TABLE II

Variation in rate of oxidation of phenyltrifluoromethylcarbinol in 77.2% acetic acid with H_0

$HClO_4(M)$	H_0	k_2
3.20	−2.82	0.259
3.20	−2.82	0.250
3.20	−2.82	0.258
2.47	−2.12	0.0433
2.47	−2.12	0.0440
1.83	−1.40	0.0059
1.83	−1.40	0.0066

EXPERIMENTAL

Reagents

Many of the fluoro alcohols had previously been synthesized in this laboratory (2, 29). During the present investigation several of these compounds were resynthesized and good agreement with all the reported physical constants was found except in the case of *m*-nitrophenyltrifluoromethylcarbinol where the melting point was found to be 51–52° instead of the reported 47–48°. The preparation of other alcohols which were synthesized specially for this investigation are given below.

m-Tolyltrifluoromethylcarbinol

m-Bromotoluene (Eastman Organic Chemicals) (49 g, 0.286 mole) and magnesium (7 g, 0.286 mole) were converted to the Grignard reagent under anhydrous conditions. Then trifluoroacetic acid (10.5 g, 0.092 mole) in 25 ml of ether was added dropwise over a period of 2 hours. After refluxing for 1 hour the complex was decomposed in 10% sulphuric acid. The product (*m*-tolyltrifluoromethyl ketone) was extracted from the aqueous solution with ether, dried over anhydrous magnesium sulphate, and distilled. B.p. 58° at 8 mm. Yield: 8.5 g, 49%. ν_{max} (liq) 1717 cm^{-1} (C=O).

This ketone (6.0 g, 0.032 mole) was dissolved in 20 ml of dry ether and lithium aluminum hydride (0.38 g, 0.01 mole) in 20 ml of dry ether was added slowly under anhydrous conditions. After refluxing for 1 hour the complex was decomposed with dilute sulphuric acid and the product was extracted with ether, washed with water, and dried over anhydrous magnesium sulphate. Distillation yielded 3.5 g (57%) of *m*-tolyltrifluoromethylcarbinol. B.p. 95° at 14 mm. (Found: C, 57.0%; H, 3.6%. $C_9H_7OF_3$ requires: C, 57.4%; H, 3.7%.)

p-tert-Butylphenyltrifluoromethylcarbinol

Starting from *p*-*tert*-butylbromobenzene *p*-*tert*-butylphenyltrifluoromethylcarbinol (m.p. 75.0–75.5°) was prepared by the same procedure used to synthesize *m*-tolyltrifluoromethylcarbinol. (Found: C, 61.6%; H, 6.13%. $C_{12}H_{15}OF_3$ requires: C, 62.0%; H, 6.52%.)

β-Naphthyltrifluoromethylcarbinol

Magnesium (2.4 g, 0.1 mole) was placed in a flame-dried three-necked flask fitted with two dropping funnels, a reflux condenser, and a magnetic stirrer. Methyl iodide (0.5 g) dissolved in 10 ml of dry ether was added through the first funnel and after the reaction had started β-bromonaphthalene (13 g, 0.063 mole) dissolved in 50 ml of dry ether was added slowly. The mixture was refluxed for ½ hour after which 100 ml of dry ether was added. This was followed by the dropwise addition of trifluoroacetic acid (1.82, g 0.016 mole) dissolved in 20 ml of dry ether. After the addition was complete the solution was refluxed for 2 hours and then decomposed with cold dilute sulphuric acid, extracted with ether, and dried. The product (β-naphthyltrifluoromethyl ketone) was distilled under reduced pressure (b.p. 88° at 1.1 mm) and crystallized from low boiling petroleum ether. ν_{max} ($CHCl_3$) 1706 cm^{-1} (C=O). Yield: 5.0 g, 0.013 mole, 80%.

This ketone (2.5 g, 0.011 mole) was reduced with lithium aluminum hydride (0.25 g, 0.0066 mole), yielding, after recrystallization from petroleum ether, a fine white crystalline compound. M.p. 83–84°. A mixed melting point with naphthalene gave a depression of 20°. (Found: C, 63.4%; H, 3.64%. Required for $C_{12}H_9OF_3$: C, 63.76%; H, 4.01%.)

p-Chlorophenyltrifluoromethylcarbinol

Starting from 1-bromo-4-chlorobenzene *p*-chlorophenyltrifluoromethylcarbinol (b.p. 117–119° C at 22 mm) was prepared by the same procedure used to synthesize *m*-tolyltrifluoromethylcarbinol. (Found: C, 44.9%; H, 2.63%. Required for $C_8H_6OF_3Cl$: C, 45.6%; H, 2.87%.)

m-Nitrophenyltrifluoromethylcarbinol-α-d

m-Nitrophenyltrifluoromethyl ketone (29) was reduced with lithium diethoxyaluminodeuteride using the procedure developed by Brown and Tsukamoto (30). This produced a brown oil which distilled at 122° at

0.4 mm. This product was recrystallized several times from benzene and petroleum ether to give pale yellow crystals. M.p. 51.5–52.5°. (Found: C, 43.1%; H, 2.00%; N, 6.28%. Required for $C_8H_5DNO_3F_3$: C, 43.2%; H, 2.72%; N, 6.32%.)

3,5-Dinitrophenyltrifluoromethylcarbinol

Fuming nitric acid (sp. gr. 1.15) was added dropwise to a stirred solution of trifluoroacetophenone (Columbia Organic Chemicals) (38.4 g, 0.216 mole) in 150 ml of concentrated sulphuric acid. External cooling was applied to maintain a temperature of 60–80° during the addition. The mixture was then heated on a steam bath for 4 hours. This was followed by cooling and the addition of another 40 ml of fuming nitric acid. The mixture was again heated on a steam bath for 4 hours and finally at 130–150° for 4 hours. The reaction mixture was then poured into crushed ice and extracted with ether. The ethereal extract was dried over anhydrous magnesium sulphate and evaporated leaving a yellow oil which was distilled under reduced pressure. The distillation yielded 2 g forerun, 10.6 g *m*-nitrophenyltrifluoromethyl ketone (b.p. 90° at 0.95 mm) and 3,5-dinitrophenyltrifluoromethyl ketone (b.p. 120–127 at 0.95 mm) (32.4 g, 0.123 mole, 57%). $\nu_{\max}$ (film) 1733 cm^{-1} (C═O). Hydrolysis of this compound with dilute sodium hydroxide yielded 3,5-dinitrobenzoic acid (m.p. 203–205°, lit. 204–205°).

Attempted recrystallization of the crude 3,5-dinitrophenyltrifluoromethyl ketone from most common solvents such as ether, petroleum ether, and chloroform yielded a stable white solid which showed no carbonyl band in the infrared, but exhibited peaks at 3490 and 3270 cm^{-1} (m.p. = 85.0–85.5°). It was concluded that this compound was 3,5-dinitrophenyltrifluoromethyl ketone hydrate. (Found: C, 32.52%; H, 2.13%; N, 9.22%. Required for $C_8H_5N_2O_6F_3$: C, 34.01%; H, 1.78%; N, 9.94%.) The analysis is hardly satisfactory, however, and despite the sharp melting point the compound may be impure. The N.M.R. spectra is consistent with the hydrate assignment as is the facile hydrolysis to 3,5-dinitrobenzoic acid which occurs in dilute sodium hydroxide.

Dehydration of 3,5-dinitrophenyltrifluoromethyl ketone hydrate by phosphorous pentoxide at 50° yielded the corresponding ketone (m.p. 77–78°). $\nu_{\max}$ ($CHCl_3$) 1737 cm^{-1} (C═O). (Found: C, 35.8%; H, 1.28%; N, 10.27%. Required for $C_8H_3N_2O_5F_3$: C, 36.4%; H, 1.14%; N, 10.60%.)

Recrystallization of the crude 3,5-dinitrophenyltrifluoromethyl ketone from ethanol yielded a white crystalline compound (m.p. 70–71°) which showed no absorption in the carbonyl region of the infrared spectra nor any in the region from 3200 to 3500 cm^{-1}, where the hydrate absorbs. (Found: C, 29.85%; H, 1.53%; N, 10.96%; O, 26.35%; F, 0.00%; m.w. = 243.) This compound was resistant to basic hydrolysis and as yet its exact structure has not been determined.

3,5-Dinitrophenyltrifluoromethylcarbinol was prepared from crude 3,5-dinitrophenyltrifluoromethyl ketone by reduction with lithium tri-*t*-butoxyaluminohydride in diglyme (31). Distillation of the yellow oil which resulted from this reaction yielded 3,5-dinitrophenyltrifluoromethylcarbinol (b.p. 108–174° at 8 mm) (9.2 g, 63%). This product was further purified by recrystallization from carbon tetrachloride. The resulting fine white crystalline compound gave an infrared spectrum similar to *m*-nitrophenyltrifluoromethylcarbinol and a nuclear magnetic resonance spectrum consistent with the assumed structure (m.p. 76–77°). (Found: C, 36.16%; H, 1.72%; N, 10.54%. Required for $C_8H_3N_2O_5F_3$: C, 36.10%; H, 1.89%; N, 10.53%.)

3,5-Dinitrophenyltrifluoromethylcarbinol-α-d

This compound was prepared by the reduction of 3,5-dinitrophenyltrifluoromethyl ketone with lithium tri-*t*-butoxyaluminodeuteride as described above (m.p. 76.8°). (Found: C, 36.07%; H, 1.78%; N, 10.78%. Required for $C_8H_2DN_2O_5F_3$: C, 36.00%; H, 1.89%; N, 10.50%.) The nuclear magnetic resonance spectrum was also consistent with the assignment of this structure.

Kinetic Methods

Oxidation rates were obtained by following the disappearance of Cr^{VI}. A plot of the reciprocal of $[Cr^{VI}]$ against time yielded the second-order rate constant directly.

Good straight line plots to at least 70% completion were obtained for all rate constants reported (Fig. 4).

Typical kinetic runs were carried out as follows: 50 ml of a 4.035×10^{-3} *M* acetic acid solution of phenyltrifluoromethylcarbinol was mixed with 20 ml of 71% perchloric acid and thermostated at 25.0±0.1° for 10 minutes. A fast-delivery pipette was then used to add 4.94 ml of 0.01361 *M* potassium dichromate to this solution and 4.92 ml aliquots were withdrawn at intervals. The aliquots were quenched by adding them to 15 ml of 5% sodium bicarbonate solution containing a large excess of potassium iodide. Two milliliters of 6 *M* sulphuric acid was added and the solution was set aside to develop for 3 minutes. The iodine formed was then titrated with standardized thiosulphate using Thyodene as an indicator.

The magnitude of the equilibrium constant in dilute aqueous solutions is such that the amount of chromium in the bichromate form is appreciable only at fairly high concentrations and Westheimer has observed that in dilute solutions (0.0005–0.005 *M*) the rate is proportional to the gross Cr^{VI} concentration (10). Although no further investigation of this equilibrium was conducted during the present work, an attempt to minimize any deviations arising from this effect was made by using concentrations of Cr^{VI} that were always lower than 0.005 *M* and in cases where rates were used for comparison purposes attempts were made to keep the Cr^{VI} concentration constant throughout the whole series.

Product Analysis

It is well known that chromic acid oxidizes most secondary alcohols smoothly to the corresponding ketones with little or no carbon–carbon bond fission (10; see, however, ref. 32). Since the concentration of

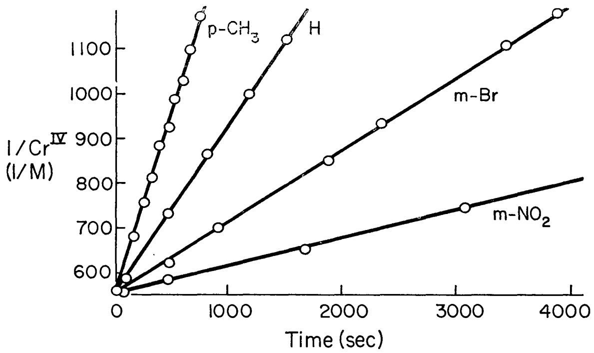


FIG. 4. Typical second-order rate plots for the oxidation of aryltrifluoromethylcarbinols in 77.2% acetic acid.

reactants was low in all of the kinetic experiments conducted in this investigation, it was found to be extremely difficult to isolate and identify the products of these reactions. However, when the concentrations of the reactants were increased to a preparative scale it was found that the aromatic alcohols gave almost quantitative yields of the corresponding ketones. The good second-order rate plots obtained also indicate that few side reactions are taking place.

ACKNOWLEDGMENT

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