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THE KINETICS OF THE CHROMIC ACID OXIDATION OF DIPHENYLMETHANE*

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Abstract—The kinetics of the chromic acid oxidation of diphenylmethane in aqueous acetic acid solution has been studied. The rate law is

$$v = k[\phi CH_2\phi][CrO_3]h_0$$

a kinetic isotope effect, $k_H/k_D = 6{\cdot}4$ at 30°, was noted, and electron releasing groups were found to moderately facilitate the reaction ($\rho^+ = -1{\cdot}17$). These, and related data, suggest that the initial reaction is the abstraction of a hydrogen atom forming a benzhydryl radical. The latter may then be further oxidized to give the product, benzphenone. It is noted that the chromic acid oxidations which must involve hydrogen abstraction all show a kinetic dependence on the total chromium (VI) concentration, whereas those which are believed to proceed via an ester mechanism have a kinetic dependence on only the acid chromate ion. This difference is suggested as a possible method of distinguishing between these two mechanisms. The effect of the water content of the solvent on the rate of the reaction is discussed, and a tentative, relative, H_- scale for some of these solutions is suggested. This may permit one to determine the number of molecules of water which are involved in a reaction.

INTRODUCTION

IN recent years, there has been considerable interest in the mechanisms of the chromic acid oxidation of organic compounds. One of the most important series of reactions of this type is that which converts a saturated hydrocarbon to a carboxylic acid or a ketone. In the case of the oxidation of a methyl group, this may occur via the alcohol and the aldehyde as intermediates, and much is known about the mechanism of oxidation of these compounds. Westheimer[1] *et al.* have investigated the chromic acid oxidation of isopropyl alcohol in considerable detail, and other workers have investigated different alcohols, obtaining similar results,[2] which are that the rate law in aqueous solution is

$$v = k_a[ROH][HCrO_4^-][H^+] + k_b[ROH][HCrO_4^-][H^+]^2$$

the reaction shows a kinetic isotope effect, $k_H/k_D = 6{\cdot}6$, when the α-hydrogen is replaced by a deuterium; manganous ion reduces the rate of reaction by a factor of

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† National Science Foundation Predoctoral Fellow, 1958–59.

[1] A. Leo and F. H. Westheimer, *J. Amer. Chem. Soc.* **74**, 4383 (1952); M. Cohen and F. H. Westheimer, *Ibid.* **74**, 4387 (1952); F. Holloway, M. Cohen and F. H. Westheimer, *Ibid.* **73**, 65(1951); F. H. Westheimer and N. Nicolaides, *Ibid.* **71**, 25 (1949); W. Watanabe and F. H. Westheimer, *J. Chem. Phys.* **17**, 61(1949); F. H. Westheimer and A. Novick, *Ibid.* **11**, 506 (1943).

[2] J. Cornforth and G. Popják, *Nature, Lond.* **164**, 1053 (1949); L. Kaplan and B. Hodnett, *Abstracts of Papers presented at the 125th Meeting, Amer. Chem. Soc., Kansas City*, p. 26N American Chemical Society (1954); V. Anthony and A. C. Chatterji, *Z. Anorg. Chem.* **280**, 110 (1955); H. Kwart and P. S. Francis, *J. Amer. Chem. Soc.* **77**, 4907 (1955).

two (when the precipitated manganese dioxide is filtered off before analysis); and one manganese dioxide is formed for each two molecules of acetone formed, when manganous ion is present.

These data show that the α-hydrogen is removed in the rate determining step, and strongly suggest that the chromium species formed in this step is Cr(IV). The further observation that a chromate ester of isopropyl alcohol may be prepared, and that it decomposes readily to acetone, led to the suggestion that the ester was formed as an intermediate in the reaction. The mechanism formulated by Westheimer is

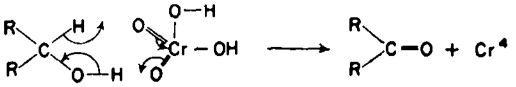
$$R_2CHOH + HCrO_4^- + H \rightleftharpoons R_2CHOCrO_3H + H_2O$$

$$R_2CHOCrO_3H + H^+ \rightleftharpoons R_2CHOCrO_3H_2^+$$

$$R_2CHOCrO_3H_2^+ + H_2O \longrightarrow R_2C{=}O + Cr(IV) + H_3O^+$$

The ester itself may also react, thus accounting for the term in the rate expression involving only one proton.

This mechanism has been attacked by Roček[3] on the grounds that the rate of reaction follows h_0 in solutions containing 5–70 per cent sulphuric acid. The application of the Hammett-Zucker hypothesis[4] then suggests that a molecule of water is not involved in the rate determining step. Roček suggested the following mechanism for the



reaction. However, as pointed out by Graham and Westheimer,[5] this is not a valid criticism, for if one writes out the entire rate expression for the Westheimer mechanism and that for the Roček mechanism, including the activity coefficients, it becomes apparent that the two are identical except for a possible difference in the activity coefficients for the two activated complexes. Thus, they probably should follow the same function of acidity, regardless of which it may be. This arises because water is formed in the first equilibrium step of the ester mechanism, and the activity of water therefore appears in the denominator of the expression for the equilibrium constant. The activity of water thus introduced will cancel the activity of water which is in the rate expression as a result of the last equation.

The above data do not allow one to decide between the two possible mechanisms for the oxidation of alcohols. However, some apparently definitive data has recently been reported by Westheimer *et al.*[6] They found that the rate of oxidation of isopropyl alcohol in D_2O as the solvent was 2·4 times as fast as the reaction in water under conditions where the kinetic dependence on acid concentration was of the first order. Many examples are known of a rate enhancement of an acid catalysed reaction by changing from H_2O to D_2O.[7] This effect results from the greater acidity of D_3O^+ as compared to H_3O^+, and a consequent higher concentration of the conjugate acid of the organic substrate in the labeled solvent. The magnitude of the effect which was observed is similar to that obtained in other reactions.

If the mechanism Roček proposed were correct, an oxygen–deuterium bond

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[3] J. Roček and J. Krupička, *Coll. Czech. Chem. Comm.* **23**, 2068 (1958).
[4] L. Zucker and L. P. Hammett, *J. Amer. Chem. Soc.* **61**, 2791 (1939).
[5] G. T. E. Graham and F. H. Westheimer, *J. Amer. Chem. Soc.* **80**, 3030 (1958).
[6] R. Brownell, A. Leo, Y. W. Chang and F. H. Westheimer, *J. Amer. Chem. Soc.* In press.
[7] K. B. Wiberg, *Chem. Rev.* **55**, 713 (1955).

would be broken as part of the rate determining step in the labeled solvent, leading to a normal isotope effect which would cancel the solvent isotope effect. Since this was not observed, it appears that the hydride abstraction mechanism is probably not correct. The alternate possibility, that a hydride abstraction occurs without the cleavage of the oxygen–deuterium bond, leading to the conjugate acid of acetone, is also unlikely in view of the large difference in rate of oxidation between isopropyl alcohol and diisopropyl ether.[6]

The oxidation of isopropyl alcohol has also been studied in aqueous acetic acid as the solvent[1] and here the rate law becomes

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

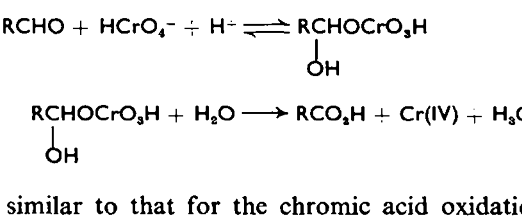
and again a kinetic isotope effect is noted. The similarity between the reaction carried out in water and that in aqueous acetic acid make it appear probable that the mechanism is the same in the two media.

The oxidation of aromatic aldehydes in aqueous acetic acid has been examined in our laboratory[8] and the oxidation of these aldehydes in aqueous solution has also been examined.[5] The rate law in the former solvent was found to be

$$v = k[\mathrm{RCHO}][\mathrm{HCrO_4^-}]h_o$$

a kinetic isotope effect, $k_H/k_D = 4{\cdot}3$, was observed when the aldehyde proton was replaced by a deuterium, and the rate of reaction was found to be reduced to one-third by the addition of manganous ion. Substituted benzaldehydes which had electron releasing groups in the *p*-positions were found to be oxidized at a slower rate than benzaldehyde, and electron withdrawing groups were found to accelerate the reaction.

Since a large kinetic isotope effect was observed, the carbon–hydrogen bond must have been broken to a considerable extent in the activated complex. If the hydrogen were removed from the aldehyde as a hydride ion, considerable acylonium ion character would be developed, and in this case, electron withdrawing substituents would be expected to accelerate the reaction, whereas the opposite was observed. The following mechanism was suggested:



$$\mathrm{RCHO + HCrO_4^- + H^+ \rightleftharpoons R\underset{OH}{C}HOCrO_3H}$$

$$\mathrm{R\underset{OH}{C}HOCrO_3H + H_2O \longrightarrow RCO_2H + Cr(IV) + H_3O^+}$$

The mechanism is similar to that for the chromic acid oxidation of isopropyl alcohol, and it has a direct analogy with the acid catalyzed permanganate oxidation of benzaldehyde for which we have proposed a similar type of mechanism.[9] For the permanganate oxidation, the rate law was found to be

$$v = k[\mathrm{RCHO}][\mathrm{MnO_4^-}][\mathrm{HA}]$$

a kinetic isotope effect was observed, and it was found that the new oxygen present

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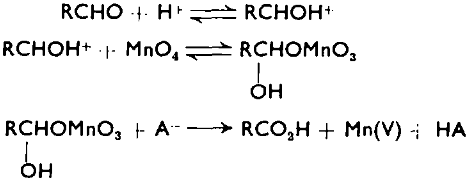
[8] K. B. Wiberg and T. Mill, *J. Amer. Chem. Soc.* **80**, 3022 (1958).

[9] K. B. Wiberg and R. Stewart, *J. Amer. Chem. Soc.* **77**, 1786 (1955).

in the product acid arose from the oxidizing agent, using O^{18} as a tracer. This required that a C–O–Mn bond be formed during the reaction, and led to the mechanism



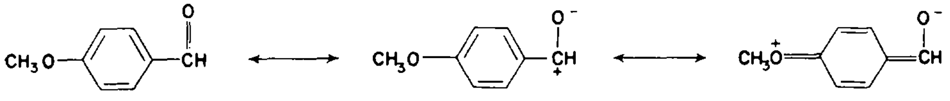
$$\mathrm{RCHO} + \mathrm{H^+} \rightleftharpoons \mathrm{RCHOH^+}$$

$$\mathrm{RCHOH^+} + \mathrm{MnO_4} \rightleftharpoons \underset{\substack{|\\ \mathrm{OH}}}{\mathrm{RCHOMnO_3}}$$

$$\underset{\substack{|\\ \mathrm{OH}}}{\mathrm{RCHOMnO_3}} + \mathrm{A^-} \longrightarrow \mathrm{RCO_2H} + \mathrm{Mn(V)} + \mathrm{HA}$$

This mechanism accounts for general acid catalysis, the observed isotope effect, and the oxygen transfer. It might be noted that this is the only one of the above reactions in which there has been obtained direct evidence for an ester being an intermediate in the reaction which gives the product and for the necessity for the involvement of a basic species.

The value of ρ, $-0{\cdot}25$, which was observed in this reaction, is of some interest. It would be valuable to have an estimate of the magnitude of ρ for the rate determining step. Unfortunately, the effect of substituents on the hydration of benzaldehyde, which should show similar effects as the equilibrium giving the permanganate ester has not been studied. An estimate may be made on the following basis. *p*-Methoxybenzaldehyde will be stabilized by the contribution of dipolar structures involving the methoxy group:



However, this type of stabilization will not be present in the hydrate, and thus the hydration of *p*-methoxybenzaldehyde will occur to a smaller extent than that of benzaldehyde. Similarly, *p*-nitrobenzaldehyde will be hydrated to a greater extent than benzaldehyde. This type of an effect should be at least as large as that on the ionization of benzoic acids, and consequently, ρ should be at least $+1$. This conclusion is supported by the observation that in the addition of hydrogen cyanide to aromatic aldehydes, ρ was found to be $1{\cdot}49$.[10]

The value of ρ for the prior equilibrium, which will be assumed to be approximately unity, must be subtracted from the observed ρ to give that for the rate controlling step. The value is, then, approximately $-1{\cdot}3$, showing that a reaction in which proton abstraction occurs may still have a considerable negative ρ. There are two possible explanations for this. First, if the activated complex resembles the products, and this is reasonable in view of the large kinetic isotope effect which was observed, then the resonance stabilization of the acid by groups such as methoxy would be important in the activated complex. This would lead to a faster reaction with a methoxy substituent, and a slower reaction with a nitro substituent. Second, electron withdrawal by manganese may be the most important electronic effect in the activated complex, so that whereas the hydrogen is being removed without its pair of electrons, the carbon is still electron deficient. It is very possible that both effects are operative.

If one considers the chromic acid oxidation in the same way, the value of ρ for

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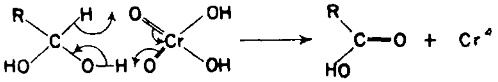
[10] H. H. Jaffé, *Chem. Rev.* 53, 191 (1953).

the rate determining step becomes approximately zero, and thus substituents have a very small effect on the rate. This again is reasonable, since a smaller kinetic isotope effect was observed here than in the permanganate oxidation (4·3 and 7·2 respectively). Thus the activated complex for the chromic acid oxidation resembles the products of the reaction to a smaller degree than that for the permanganate oxidation, and consequently the effect of substituents should be smaller.

Roček[11] has recently presented evidence which he interpreted as favoring an alternate mechanism for the oxidation of aldehydes. He found that the rates of oxidation of the hydrates of chloral, dichloroacetaldehyde, chloroacetaldehyde and of acetaldehyde increased in that order, the rates being correlated with σ^* with a ρ^* of $-1{\cdot}2$. He then suggested that it was more reasonable to propose a hydride abstraction than a proton abstraction in view of the sign of ρ^* and suggested the following mechanism



He also argued that it was the hydrate of the aromatic aldehydes which was oxidized by chromic acid, and since the ρ for the hydration equilibrium must be positive, the data which we obtained on the effect of substituents would not serve to rule out the above mechanism for these compounds also.

The discussion presented above indicates that the sign of ρ cannot be used in deciding between hydride abstraction and proton abstraction, and in view of the results obtained in the permanganate oxidation, one would expect a negative ρ for the case which was studied by Roček. Thus, his results are in accord with *either* mechanism. Roček's mechanism can be shown to be probably incorrect by comparing the rates of oxidation of acetaldehyde in water and in deuterium oxide. In the region of acid concentration which gave second order dependence on the latter, the solvent isotope effect, k_{D_2O}/k_{H_2O}, was 6·29.[12] This may be compared with the corresponding isotope effect in the oxidation of isopropyl alcohol, $k_{D_2O}/k_{H_2O} = 6{\cdot}26$.[6] As in the oxidation of isopropyl alcohol, if an oxygen–deuterium bond were cleaved in the rate determining step, as is required by Roček's mechanism, the solvent isotope effect would be reduced by a factor corresponding to the normal isotope effect for the cleavage of this bond. The observed value is, however, normal for reactions involving two protons prior to the rate determining step.[6,7] Therefore, it seems unlikely that the hydride abstraction mechanism is correct. The mechanism involving an ester intermediate will accommodate these observations, and also receives further support by the data to be presented in the discussion section on the nature of reactions which have a kinetic dependence on only the acid chromate ion.

The oxidation of hydrocarbons is considerably less well understood. Slack and Waters[13] have investigated the chromic acid oxidation of diphenylmethane in glacial acetic acid and concluded that the rate law was

$$v = k[\phi CH_2\phi][CrO_3]^2[H^+]^n$$

where the order with respect to the concentration of acid was not clearly defined.

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[11] J. Roček, *Tetrahedron Letters* No. 5, 1 (1959).

[12] These experiments were performed by Dr. William Richardson, and will be reported in detail in another connection.

[13] R. Slack and W. A. Waters, *J. Chem. Soc.* 599 (1949).

The kinetic order with respect to the stoichiometric concentration of chromium trioxide was not too well established since it was based on the kinetic behavior during an experiment, rather than on the effect of chromium trioxide concentration on the rate constant.

They proposed a mechanism involving the attack of two molecules of chromic acid on the hydrocarbon in the rate controlling step to form a species having two chromium–carbon bonds, with subsequent rearrangement to a structure similar to that proposed for an Etard complex. A small amount of tetraphenylethane was obtained from the reaction, but the formation of this compound was attributed to a side reaction, rather than being an indication of a process involving free benzhydryl radicals.

The oxidation of toluene and some substituted toluenes have been investigated by Ogata *et al.*[14] They assumed a rate law corresponding to that of Slack and Waters, and observed that electron withdrawing groups retarded the reaction.

Very few aliphatic hydrocarbons have been studied. Sager and Bradley[15] found that triethylmethane was oxidized in aqueous acetic acid to give triethylcarbinol as a major initial product, which then reacted further by dehydration and oxidation of the olefin thus formed. Roček[16] has obtained similar results in the oxidation of methylcyclohexane. The rate determining step was shown by Sager and Bradley to be the abstraction of the tertiary hydrogen since a kinetic isotope effect was observed when the tertiary hydrogen was replaced by a deuterium.

These data do not, however, indicate whether the hydrogen was removed as a hydride ion or as a hydrogen atom. In the former case, a carbonium ion would be formed, which would be hydrated to form the alcohol. This would also account for the simultaneous formation of 3-pentanone since the carbonium ion would also lose a proton, giving the olefin which would in turn be rapidly oxidized to the ketone. If a hydrogen atom were removed, a tertiary free radical would be formed, which would then probably react with the oxidizing agent, either by an electron exchange reaction giving the carbonium ion, or by adding to the chromic acid to give a chromium(V) ester which could be hydrolyzed to the tertiary alcohol.

It can be seen that whereas the oxidation of alcohols and of aldehydes is fairly well understood, the oxidation of hydrocarbons requires considerable further study. The results of an investigation of one hydrocarbon, diphenylmethane, is the subject of the present work.

EXPERIMENTAL

Materials. Diphenylmethane was a commercial grade which was distilled twice giving material melting at 27°. The *p*-chloro, *m*-chloro, *p*-bromo, *m*-methoxy, *p,p'*-dimethoxy, *p*-methyl, *p,p'*-dimethyl and *p,p'*-dichlorodiphenylmethanes were prepared from the corresponding ketones by the Huang-Minlon[17] modification of the Wolff-Kishner reduction. Each of the substituted hydrocarbons was purified by chromatography over alumina followed by distillation or recrystallization.

Diphenylmethane-d_2 was prepared by the lithium aluminum deuteride reduction of dichlorodiphenylmethane.[18] To a suspension of 1 g lithium aluminum deuteride in 25 ml tetrahydrofuran maintained at reflux temp was added a solution of 6·1 g dichlorodiphenylmethane in 25 ml tetrahydrofuran over a period of 5 hr, with stirring. The solution was heated for an additional ½ hr, and then

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[14] Y. Ogata, A. Fukui and S. Yuguchi, *J. Amer. Chem. Soc.* **74**, 2707 (1952).

[15] W. F. Sager and A. Bradley, *J. Amer. Chem. Soc.* **78**, 1187 (1956).

[16] J. Roček, *Coll. Czech. Chem. Comm.* **22**, 1509, 1519 (1957).

[17] Huang-Minlon, *J. Amer. Chem. Soc.* **68**, 2487 (1946).

[18] W. W. Kaeding and L. J. Andrews, *J. Amer. Chem. Soc.* **74**, 6189 (1952).

cooled and added to a mixture of ice and sulfuric acid. The organic material was taken up in ether, and the ether layer was separated and dried. Evaporation of the solvent gave 5 g yellow oil which was chromatographed over 50 g alumina, using petroleum ether for elution. Evaporation of the resultant solution and distillation gave 2·5 g diphenylmethane-d_2, b.p. 96–97° at 3 mm. The material used in the kinetic runs was repurified by chromatography, and was shown to have an insignificant amount of unlabeled and mono-deuterium labeled diphenylmethane by the absence of the methylene proton resonance bands in the NMR spectrum.

p-Methoxydiphenylmethane-d_2 was prepared by the reduction of *p*-methoxybenzophenone with lithium aluminum deuteride and aluminum chloride, using the procedure previously reported using lithium aluminum hydride.[19]

The inorganic compounds were of a reagent grade. The acetic acid was purified as described previously[8] and was diluted with water to give 95 % acetic acid by weight. The 91 % acetic acid is the solvent used previously.[8]

Kinetic and analytical method. The procedures used were identical with those previously reported in the study of the chromic acid oxidation of benzaldehyde.[8]

Product analysis. In several cases, the stoichiometry of the reaction was determined using product analyses. The reactions were carried out in a manner similar to the kinetic experiments (using an excess of diphenylmethane) and were allowed to proceed to completion. The reaction mixture was diluted with ice-water which had been saturated with salt, and was extracted several times with ether. The ether solution was washed with water, dried over sodium sulfate and evaporated under reduced pressure. The material thus obtained was chromatographed over alumina, the diphenylmethane being eluted with petroleum ether and the benzophenone being eluted with 1:3 ether–petroleum ether. In each case, only diphenylmethane and benzophenone were isolated. In no case was any tetraphenylethane obtained, although it was shown that it could have been isolated if it were present.

Monomer–dimer equilibrium constant in 95 % acetic acid

The equilibrium constant for the reaction

$$2\ HCrO_4^- \rightleftharpoons Cr_2O_7^{2-}\ (+H_2O)$$

was estimated by comparing the spectra of chromium trioxide at various concentrations in 91 % and 95 % acetic acd. The equilibrium constant had been determined to be 25 for 91 % acetic acid using the deviation from Beer's Law,[8] and it can be seen from Fig. 1 that the deviation starts at a lower concentration of chromium trioxide when 95 % acetic acid is the solvent. The concentrations of chromium trioxide which give the same concentration of the dichromate ion will be given by points of equal slope for the two curves. These points are separated by 0·20 ± 0·05 log units, corresponding to a ratio of concentrations of 1·6 ± 0·2. Thus, the equilibrium constant is 65 ± 15 in 95 % acetic acid.

RESULTS

The use of glacial acetic acid as the solvent for this oxidation is not desirable because of the low solubility of chromium trioxide, the difficulty in obtaining and working with pure, anhydrous acetic acid, and the lack of knowledge concerning the nature of the chromium species present in the solution. We have previously determined the acidity function, H_0, for perchloric acid in aqueous acetic acid solutions[20] and a value for the acid chromate–dichromate equilibrium constant was determined in 91 per cent acetic acid.[8] Therefore aqueous acetic acid was chosen as the solvent. The reaction proceeded at a rather low rate in 91 per cent acetic acid, and so, a 95 per cent solution was chosen for most of the kinetic experiments.

Since it appears that oxidation of the solvent may occur during the reaction,[14] the stoichiometry was examined first. The oxidation of diphenylmethane (0·036 M) with chromic acid (0·0124 M) in the presence of 0·045 M perchloric acid was effected at 30°, and the diphenylmethane and benzophenone were separated by chromatography

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[19] R. F. Nystrom and C. R. A. Berger, *J. Amer. Chem. Soc.* **80**, 2896 (1958).

[20] K. B. Wiberg and R. J. Evans, *J. Amer. Chem. Soc.* **80**, 3019 (1958).

over alumina. Only 84 per cent of the theoretical amount of diphenylmethane was oxidized and 87 per cent of benzophenone, based on diphenylmethane used, was obtained. Since aromatic rings are usually not easily attacked under these conditions, it appeared that the deficiency in the amount of diphenylmethane oxidized might be attributed to the oxidation of the solvent. This oxidation could not be affected by Cr(VI) since solutions of chromic acid in this solvent are stable for long periods at the temperature used. However, oxidation by Cr(V) or (IV), which may be formed as intermediates in the oxidation, may occur.

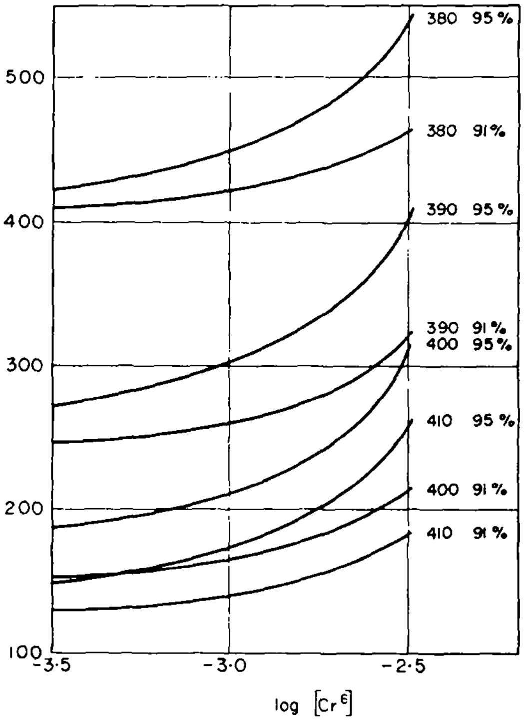

FIG. 1. Deviation from Beer's law for solutions of chromium trioxide in 91 per cent and 95 per cent acetic acid-water mixtures.

It is known that cerous ion and manganous ion react rapidly with Cr(V) and Cr(IV), whereas they react very slowly with Cr(VI).[21] The addition of cerous ion should then remove these species and should suppress the induced oxidation of the solvent. When the above experiments was repeated in the presence of 0·0038 M cerous ion, 98 per cent of the theoretical amount of diphenylmethane was used, and 86 per cent of the theoretical amount of benzophenone was isolated. A similar result was obtained when manganous ion was used. Thus, the non-stoichiometry of the reaction is largely due to induced oxidation, probably of the solvent, involving Cr(IV) or (V). In order to suppress this, all of the kinetic experiments were carried out using a considerable excess of diphenylmethane.

Oxygen is known to have an effect on chromic acid oxidations. Waters[22] has

[21] F. H. Westheimer, *Chem. Rev.* **45**, 419 (1949).

[22] W. Waters, *J. Chem. Soc.* 1151 (1946); R. Luther and T. F. Rutter, *Z. Anorg. Chem.* **54**, 1 (1907), for an example in which only inorganic reagents are involved.

noted absorption of oxygen in several cases, and in the oxidation of benzaldehyde in 91 per cent acetic acid, we have noted that the rate of disappearance of chromic acid is somewhat greater than the rate of disappearance of benzaldehyde when the reaction is carried out under nitrogen ($k_{\mathrm{Cr}^6}/k_{\phi\mathrm{CHO}}$ = 1·1), presumably due to a small amount of induced oxidation of the solvent, but that the reverse is true when the reaction is carried out under oxygen ($k_{\mathrm{Cr}^6}/k_{\phi\mathrm{CHO}}$ = 0·92). Furthermore, the rate of reaction was approximately halved in the presence of oxygen.

The effect of oxygen was therefore determined in the oxidation of diphenylmethane.

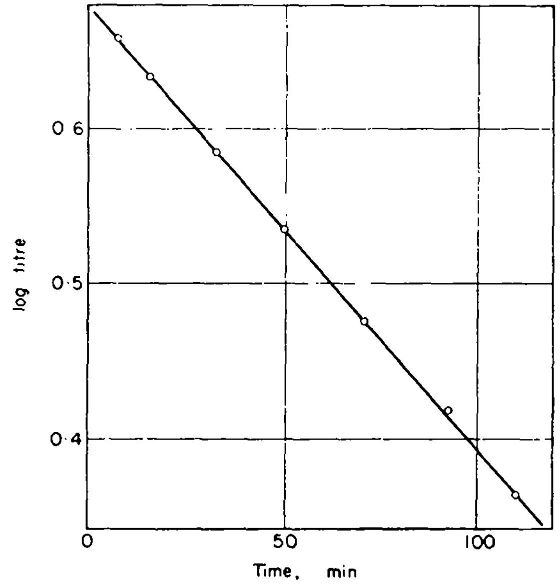

FIG. 2. Typical first order rate plot for the oxidation of diphenylamine.

The rate of reaction (followed by disappearance of chromic acid) was decreased to about 60 per cent of the value obtained in the absence of oxygen, and the effect on the rate was not significantly different when the reaction was carried out in the presence of air, or by bubbling oxygen through the solution. The stoichiometry was examined for the case in which oxygen was bubbled in, and it was found that 105 per cent of the theoretical amount of diphenylmethane was oxidized, and 90 per cent of benzophenone (based on diphenylmethane used) was obtained. All subsequent reactions were carried out in an atmosphere of nitrogen.

Each kinetic run, under these conditions, fitted a first order rate expression for the disappearance of chromic acid. A typical first order plot is given in Fig. 2. The rate of reaction as a function of the diphenylmethane concentration was determined over a 12-fold range of the latter. The second order rate constants which were calculated were constant (Table 1) indicating the reaction to be first order with respect to diphenylmethane.

The order with respect to perchloric acid was determined in the same way. A plot of log k against log $[\mathrm{H}^+]$ gave a linear relationship with a slope of 1·27. A similar plot against H_0 gave a straight line with a slope of −1·05 (Fig. 3). A consideration of the effect of the water concentration in the solvent on the rate reaction (see below)

TABLE 1. EFFECT OF DIPHENYLMETHANE CONCENTRATION OF THE RATE OF CHROMIC ACID OXIDATION

[Diphenylmethane]	$k_1 \times 10^4$ (sec^{-1})	$k_2 \times 10^4$ (1 mole^{-1} sec^{-1})
0·400 M	2·35	5·87
0·250	1·38	5·52
0·200	1·05	5·25
0·150	0·833	5·55
0·100	0·617	6·17
0·050	0·269	5·38
0·030	0·175	5·83
		Ave 5·65 ± 0·26

$[HClO_4] = 0{\cdot}133$ $[Cr^6] = {\cdot}0030$ $[NaClO_4] = 0{\cdot}167$
95% acetic acid $T = 30°$

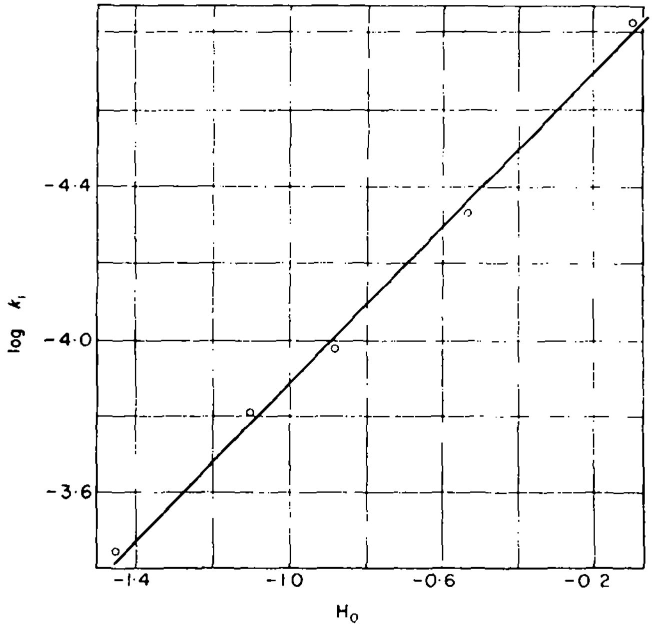

FIG. 3. Effect of acid concentration on the rate of oxidation of diphenylamine.

suggests that H_0 is a more satisfactory measure of the acidity of the medium than is the stoichiometric concentration of acid. This point has been considered previously.[8,20]

The effect of chromic acid concentration on the observed rate constants was also determined. The results are given in Tables 2 and 3. It is apparent that the rate of reaction is proportional to the total chromium (VI) concentration. It should be noted that this is not typical behavior. In the oxidation of alcohols and of aldehydes,[1,2,5,8] the rate constants were found to decrease with increasing chromium trioxide concentration. This has been attributed to the monomerdimer equilibrium found in these solutions, only the acid chromate ion being

$$2\,HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

involved in the rate expression.[1] The difference between the two cases may indicate

TABLE 2. EFFECT OF CHROMIC ACID CONCENTRATION ON ON THE OBSERVED RATE CONSTANTS IN 91% ACETIC ACID

$[Cr^6] \times 10^3$	$k_1 \times 10^4$ (sec^{-1})	$[Cr_2O_7^=]/\Sigma[Cr^6]$
36·1	3·14	0·27
30·2	3·20	0·25
22·8	3·38	0·22
15·4	3·07	0·20
7·76	2·81	0·13
3·92	2·72	0·09
1·88	3·47	0·05
0·92	3·26	0·02
0·40	3·77	0·00
	Ave 3·20 ± 0·24	

[diphenylmethane] = 0·200 $[HClO_4] = 0{\cdot}500$ $T = 37°$

TABLE 3. EFFECT OF CHROMIC ACID CONCENTRATION ON THE OBSERVED RATE CONSTANTS IN 95% ACETIC ACID

$[Cr^6] \times 10^3$	$k_1 \times 10^4$ (sec^{-1})	$[Cr_2O_7]/\Sigma[Cr^6]$
15·0	1·09	0·25
12·2	1·15	0·23
7·90	1·01	0·19
3·06	1·06	0·12
1·60	0·99	0·08
0·92	0·96	0·06
	Ave 1·04 ± ·06	

[diphenylmethane] = 0·200 $[HClO_4] = 0{\cdot}120$
$[NaClO_4] = 0{\cdot}180$ $T = 30°$

either that the equilibrium constant has a value such that only one of the two chromium species is present in the range of concentration used, or that both the acid chromate ion and the dichromate ion are effective, and the rate constant for the reaction of the latter is approximately twice that for the former.

The value for the equilibrium constant in 91 per cent acetic acid is available from our previous work, and an estimate of the change in value caused by going to 95 per cent acetic acid was determined by a comparison of the spectra of solutions of chromium trioxide of various concentrations in the two solvents. This indicated a value for the equilibrium constant of 65 ± 15 for the solvent used here. This result demonstrates that only the acid chromate ion was present in the more dilute solutions which were used, and that considerable dichromate ion was present in the more concentrated solutions. Thus it appears that both species are involved in the oxidation.

At higher chromic acid concentrations than those reported in Table 1, it was found that the rate of reaction was large to begin with, and then decreased to the normal value as the reaction progressed. It is known that polychromates may be formed,[23] and solutions which contain relatively little water should be favourable for the formation of these species. If the polychromates were for some reason particularly reactive in effecting the oxidation, then the observed results would be reasonable. The reaction would proceed relatively rapidly until the concentration of chromium (VI) had dropped to a value at which relatively little polychromate would be present in equilibrium. Then the normal rate for reaction by the acid chromate and dichromate ions would be observed.

TABLE 4. EFFECT OF SUBSTITUENTS ON THE CHROMIC ACID OXIDATION OF DIPHENYLMETHANE

Substituent	k/k_H
p,p'-Dimethoxy[a]	347
p-Methoxy[a]	91·3
p,p'-Dimethyl	6·42
p-Methyl	2·28
Hydrogen	1·00
p-Chloro	0·76
p-Bromo	0·72
p,p'-Dichloro	0·49
m-Chloro	0·40
m-Bromo	0·40

$[HClO_4] = 0·240$ $[Cr_6] = 0·0030$
$[Mg(ClO_4)_2] = 0·020$ 95% acetic acid $T = 30°$

[a] In these cases, the rate of reaction increased with increasing time. The rate constants given are based on the initial slope.

There are two possible rate determining steps for the reaction. In the first, a carbon–hydrogen bond is cleaved, and in the second, a complex is formed between the hydrocarbon and the chromium species. These may be differentiated using the kinetic isotope effect. Diphenylmethane-d_2 was prepared by the reduction of diphenyldichloromethane with lithium aluminum deuteride. The rate of reaction was found to be decreased by a factor of 6·4 ($k_2 = 10·9 \times 10^{-4}$ for the unlabeled compound, $k_2 = 1·69 \times 10^{-4}$ for the labeled material, 0·096 M R_2CH_2, 0·0030 M Cr^6, 0·240 M $HClO_4$, 0·060 M $NaClO_4$, 95 per cent acetic acid, 30°), indicating that the former is correct.

The effect of substituents was also determined, giving the data in Table 4.

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[23] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry* Vol. XI, pp. 349–351.

With the exception of the *p*-methoxy substituted compounds, all of the oxidations gave good first order plots for the disappearance of chromic acid, using a considerable excess of the diphenylmethane. Since methoxy substituted aromatic compounds are oxidized by chromic acid, the methoxy substituted diphenylmethanes will be excluded from the correlations below, and will be considered separately.

A plot of the logarithm of the relative rates of reaction against the Hammett σ values[10] gave a fair fit to a straight line with a slope of $-1{\cdot}40$. A better correlation was found in the σ^+ values of Brown and Okamoto,[24] the slope of the line being $-1{\cdot}17$ in this case (Fig. 4).

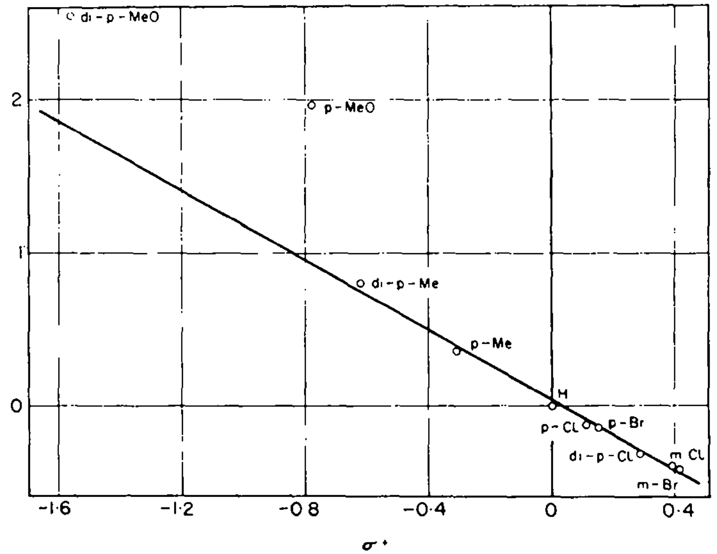

Fig. 4. Effect of substituents on the rate of the chromic acid oxidation of diphenylamine.

The water content of the solvent and the concentration of electrolyte were found to affect the rate of the chromic acid oxidation of benzaldehyde,[8] and thus data on the effect of these variables on the rate of oxidation of diphenylmethane was obtained. The results are given in Tables 5 and 6. It can be seen from the data in the former table that the dichromate ion is about twice as reactive as the acid chromate ion in all of the solutions, and that the rate of reaction of the latter is increased about 60 per cent by halving the concentration of water. It might be noted that the rate of oxidation of benzaldehyde at constant value of H_0 is independent of the water content of the medium.[8]

The enthalpy and entropy of activation were also determined. The rate constants at 20°, 30° and 40° (95 per cent acetic acid, 0·300 M $HClO_4$, 0·200 M diphenylmethane, 0·003 M Cr^6) were 1·48, 3·27 and $8{\cdot}44 \times 10^{-4}$ sec^{-1}, giving $\Delta H^{\ddagger} = 15{\cdot}2$ kcal, $\Delta S^{\ddagger} = -21{\cdot}2$ e.u.

In the studies of the oxidation of isopropyl alcohol and of benzaldehyde, an investigation of the induced oxidation of ions such as cerous and manganous during the reaction has proved helpful in defining the mechanism of the reaction. These species serve to remove the intermediate chromium species, and thereby suppress the

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[24] H. C. Brown and Y. Okamoto, *J. Org. Chem.* **22**, 485 (1957); *J. Amer. Chem. Soc.* **80**, 4980 (1958).

reactions of the latter. In water as the solvent, the induced oxidation of manganous ion leads to the formation of manganese dioxide which precipitates from the solution. However, in aqueous acetic acid as the solvent, manganese dioxide does not precipitate and since the reactions carried out in the presence of manganous ion gave good first order plots for the disappearance of oxidizing power to over two half-lives, it is apparent that Mn(III) and Mn(IV) do not accumulate in the solution to an appreciable extent. The same is also true for cerous ion.

The results of this investigation are presented in Table 7. It can be seen that in all cases, there is a marked decrease in rate, to a value between three-tenths and six-tenths that observed in the absence of these ions. Any simple treatment of this phenomenon (cf. discussion) predicts a value of one-third in the absence of a chain reaction, and thus it seems reasonable to assume a limiting value of one-third for this oxidation. The same result was previously obtained in the oxidation of benzaldehyde.[8] It should be noted that the reduction in rate is affected by both the cerous (or manganous) ion concentration, and by the acid concentration. The latter appears to be the more important when manganous ion is used. The first two entries in the table which were determined using 0·120 M perchloric acid are subject to some question, since a brown

TABLE 5. EFFECT OF WATER CONCENTRATION ON THE RATE OF THE CHROMIC ACID OXIDATION OF DIPHENYLMETHANE AT A CONSTANT VALUE OF H_0

$[Cr^6] \times 10^3$	$\%H_2O$	$[Cr_2O_7^{2-}]/\Sigma[Cr^6]$	$[HClO_4]$	$k_1 \times 10^4 sec^{-1}$
1·57	9	0·05	0·300	0·549
9·48	9	0·13	0·300	0·527
1·68	8		0·234	0·601
9·62	8		0·234	0·560
1·70	5	0·08	0·115	0·845
9·82	5	0·21	0·115	0·951
1·75	4		0·0812	0·951
9·69	4		0·0812	1·11

$H_0 = -0{\cdot}84$ [diphenylmethane] = 0·200 M
$T = 30°$ ionic strength = 0·300 M

TABLE 6. EFFECT OF SALT CONCENTRATION ON THE RATE OF OXIDATION

$[NaClO_4]$	$k_1 \times 10^4 sec^{-1}$	μ
0·00	1·95	0·160
0·048	1·78	0·208
0·080	1·61	0·240
0·240	1·51	0·400

$[HClO_4] = 0{\cdot}160$ [diphenylmethane] = 0·200 $[Cr^6] = 0{\cdot}010$
$T = 30°$ 95% acetic acid

colour [possibly Mn(III)] developed on standing when the manganous ion and chromic acid solutions were mixed. The higher acid concentration repressed the formation of this colour. It is not clear how this might effect the rate constants, but it is possible that part of the reduction in rate for these two cases is due to the reaction forming the brown colour.

It was seen previously that the *p*-methoxy substituted diphenylmethanes react with chromic acid at a rate which is much greater than that for the other compounds.

TABLE 7. EFFECT OF CEROUS AND MANGANOUS ON THE RATE OF THE CHROMIC ACID OXIDATION OF DIPHENYLMETHANE

		Cerous ion				Manganous ion			
Subst.	%HOAc	[Ce^3]	[ϕ_2CH_2]	[H^+]	k/k_0	[Mn^2]	[ϕ_2CH_2]	[H^+]	k/k_0
H	95					0·040	0·200	0·120	0·36
	95					0·023	0·200	0·120	0·42
	95					0·020	0·200	0·180	0·47
	95					0·010	0·200	0·180	0·48
	95					0·020	0·200	0·240	0·57
*p*Cl	95					0·020	0·200	0·240	0·46
	95					0·020	0·174	0·240	0·56
H	91	0·0033	0·200	0·300	0·58	0·0067	0·200	0·300	0·58
	91	0·033	0·200	0·300	0·47	0·033	0·200	0·300	0·55
	91					0·067	0·200	0·300	0·52
	91	0·0167	0·200	0·400	0·60	0·0067	0·200	0·400	0·63
	91	0·0167	0·200	0·400	0·65	0·020	0·200	0·400	0·63
*p*Cl	91	0·033	0·151	0·300	0·44	0·0667	0·151	0·300	0·47
p,*p*′-diMe	91	0·0033	0·106	0·300	0·34	0·0067	0·106	0·300	0·50
	91	0·033	0·016	0·300	0·27				

[Cr^6] = 0·0025–0·003 M

This could be due to a change in mechanism, possibly to a chain reaction, or to a change in the type of reaction. These possibilities have been examined. The stoichiometry of the oxidation of *p*-methoxydiphenylmethane was determined, and it was found that 87 per cent of the theoretical amount of the reactant was consumed and an 80 per cent yield of *p*-methoxybenzophenone based on the diphenylmethane used was obtained. The corresponding values for diphenylmethane itself were 84 per cent and 87 per cent. Thus, the site of attack is the same in both cases. The kinetic isotope effect was also determined giving $k_H/k_D = 3{\cdot}1$ ($k_0^H = 3{\cdot}66 \times 10^{-6}$ mole/l.sec.; $k_0^D = 1{\cdot}19 \times 10^{-6}$; 0·0303 M diphenylmethane, 0·060 M $HClO_4$, 0·240 M $NaClO_4$, 0·003 M Cr^6, 30°, 95 per cent acetic acid). Since we have previously shown that in any series of related reactions the kinetic isotope effect decreases as the rate of reaction increases,[25] a decrease in the isotope effect from the value observed for diphenylmethane itself (6·4) would be expected. It is clear that the rate determining step is still the cleavage of the methylene carbon–hydrogen bond.

[25] K. B. Wiberg and L. H. Slaugh, *J. Amer. Chem. Soc.* **80**, 3033 (1958).

Unlike the oxidation of diphenylmethane itself, the oxidation of the *p*-methoxy substituted derivative followed an apparent zeroth order course (Fig. 5) in the presence of excess of the latter. With *p*,*p*′-dimethoxydiphenylmethane, even the zeroth order plots showed an upward drift with time. This suggests that there is a small autocatalytic component in the reaction, and the effect of the initial chromium trioxide concentration on the zero order rate constants (Table 8) indicates that the reaction is still first order in the oxidizing agent. The rate of the reaction was also shown to be first order with respect to the concentration of *p*-methoxydiphenylmethane (Table 8).

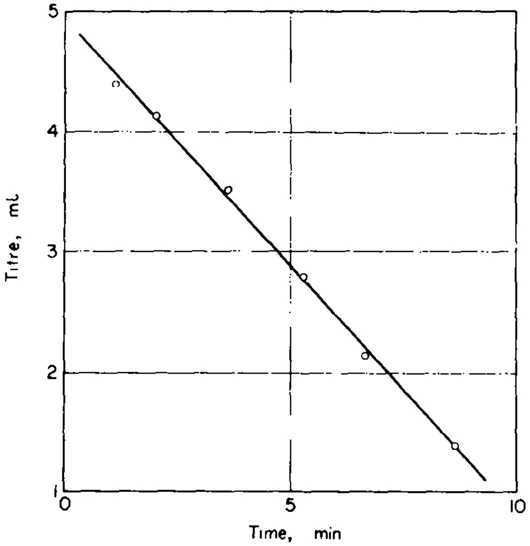


FIG. 5. Typical zero order rate plot for the oxidation of *p*-methoxydiphenylmethane.

TABLE 8. EFFECT OF THE CONCENTRATION OF THE REACTANTS ON THE RATE OF THE CHROMIC ACID OXIDATION OF *p*-METHOXYDIPHENYLMETHANE

$[Cr^6] \times 10^3$	$[R_2CH_2] \times 10^2$	$k_0 \times 10^6$ mole/l sec	$k_0/[Cr^6]$	$k_0/[R_2CH_2]$
1·74	3·33	2·29	1·31	
3·31	3·33	3·73	1·13	
6·14	3·33	6·38	1·04	
10·06	3·33	11·6	1·15	
3·31	6·67	6·92		1·04
3·31	3·33	3·73		1·12
3·33	1·33	1·40		1·05
		Ave	1·16 ± ·08	1·07 ± ·03

$[HClO_4] = 0{\cdot}060$ M $[NaClO_4] = 0{\cdot}240$ M 30° 95% acetic acid

The effect of the acid concentration on the rate of the reaction was also determined giving the data in Table 9. A plot of log k against K_0 gave a straight line of slope 1·45 for the reaction carried out in 91 per cent acetic acid, and of 1·30 for the reaction carried out in 95 per cent acetic acid. It is interesting to note that the reaction proceeded more rapidly in 91 per cent acetic acid, at a constant value of H_0, than in the 95 per cent solvent. This appears to be the first case of a chromic acid oxidation proceeding more rapidly in the more aqueous solvent.

A difference between the oxidation of *p*-methoxydiphenylmethane and other diphenylmethanes is also found in the enthalpy and enthropy of activation. The rates of reaction were determined at 20°, 30° and 40°, the rate constants being 1·21, 3·73 and 9·64 × 10^{-6} mole $l.^{-1}$ sec^{-1} (0·033 M R_2CH_2, 0·060 M $HClO_4$, 0·003 M Cr^6, 0·240 M $NaClO_4$, 95 per cent acetic acid). These values lead to $\Delta H^{\ddagger} = 17{\cdot}4$ kcal, $\Delta S^{\ddagger} = -4{\cdot}7$ e.u., which are quite different from those obtained in the oxidation of diphenylmethane ($\Delta H^{\ddagger} = 15{\cdot}2$ kcal, $\Delta S^{\ddagger} = -21{\cdot}2$ e.u.).

TABLE 9. EFFECT OF ACID CONCENTRATION AND OF SOLVENT COMPOSITION ON THE RATE OF THE CHROMIC ACID OXIDATION OF *p*-METHOXYDIPHENYLMETHANE

91% Acetic acid			95% Acetic acid		
$[HClO_4]$	H_0	$k_0 \times 10^6$	$[HClO_4]$	H_0	$k_0 \times 10^6$
0·300	−0·82	14·7	0·120	−0·86	10·3
0·200	−0·60	7·04	0·060	−0·59	3·73
0·100	−0·27	2·30	0·024	−0·14	1·17

$[Cr^6] = 0{\cdot}003$ M ionic strength = 0·300 M $T = 30°$

TABLE 10. EFFECT OF MANGANOUS AND CEROUS ION ON THE CHROMIC ACID OXIDATION OF *p*-METHOXYDIPHENYLMETHANE AND *p,p′*-DIMETHOXYDIPHENYLMETHANE

Subst.	$[R_2CH_2]$	%HOAc	$[HClO_4]$	$[Ce^3]$	$[Mn^2]$	$[NaClO_4]$	$k_0 \times 10^6$	$k_{obs}/k_{uninhib}$
*p*MeO-	0·0333	95	0·120	0	0	0·180	10·3	0·
*p*MeO-	0·0333	95	0·120	0·01	0	0·120	3·56	0·35
*p*MeO	0·0333	95	0·120	0	0·004	0·168	10·1	0·98
p, p′-diMeO	0·0125	91	0·200	0	0	0·300	0·680[a]	
p, p′-diMeO	0·0125	91	0·200	0	0·0667	0·100	1·17[a]	1·72
p, p′-diMeO	0·0125	91	0·200	0	0·0333	0·200	0·866[a]	1·27
p, p′-diMeO	0·0125	91	0·200	0	0·0067	0·280	0·758[a]	1·11
p, p′-diMeO	0·0125	91	0·200	0·0333	0	0·100	0·499[a]	0·73
p, p′-diMeO	0·0125	91	0·200	0·0033	0	0·280	0·513[a]	0·75

$[Cr^6] = 0{\cdot}0025$–$0{\cdot}003$ M [a] Initial rates

It is possible to determine if the reaction is a chain-process by examining the inhibition of the reaction by cerous or manganous ion. In any chain process, the intermediate chromium species Cr(V) and Cr(IV) would have to be chain carriers. Thus, a marked reduction in rate would be expected. The data which were obtained are summarized in Table 10.

It is interesting to note that with *p,p′*-dimethoxydiphenylmethane, manganous ion catalysed the reaction. This is unusual, but it has been observed previously, as in the oxidation of lactic acid.[26] The inhibition by cerous ion was more marked with *p*-methoxydiphenylmethane than with the disubstituted compound, in the former case the rate being reduced to near the one-third ratio which might be expected. It is clear that a chain process involving the intermediate chromium species as chain carriers is ruled out by these data.

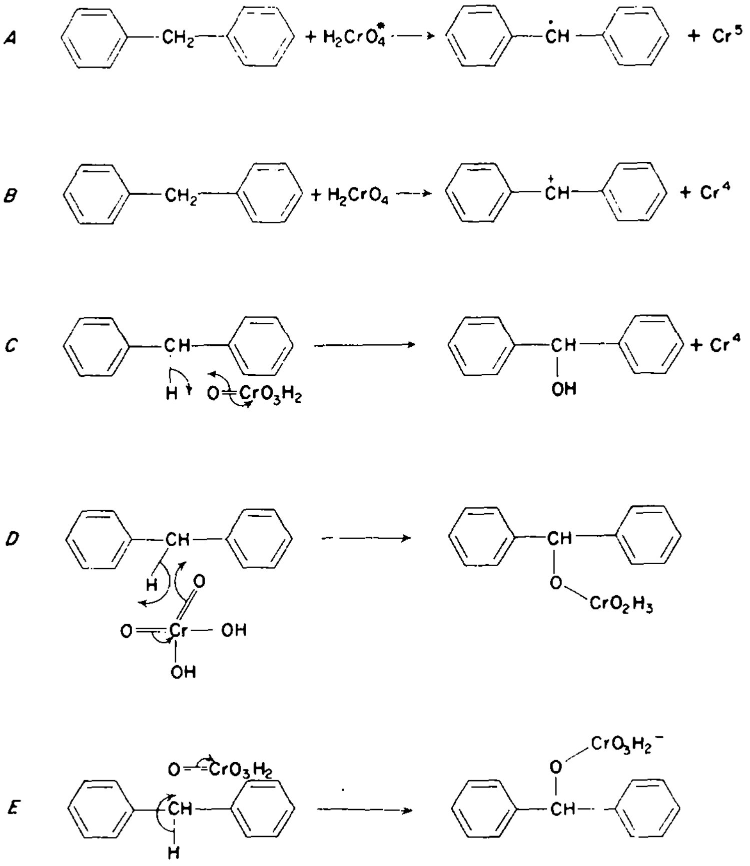
In connection with this work, the rates of reaction of a number of other hydrocarbons and their derivatives were determined. The relative rates are given in Table 11.

DISCUSSION

The observed rate law:

$$v = k[\phi CH_2\phi][CrO_3]h_0$$

suggests that the reaction may be one between diphenylmethane and a protonated species of chromium(VI). The observation of a kinetic isotope effect, $k_H/k_D = 6{\cdot}4$. indicates that the rate determining step is the cleavage of the methylene carbon-hydrogen bond. There are, then, five mechanisms by which the initial reaction may occur:



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[*] The reactant is, for convenience, written as chromic acid, although it is clear that the acid dichromate ion is also a reactant.

[26] A. N. Dey and N. R. Dhar, *Z. Elektrochem.* **32**, 586 (1926); N. R. Dhar, *Ann. Chim.* [9], **11**, 130 (1919); *J. Chem. Soc.* **111**, 707 (1917).

In the first of these, a benzhydryl radical is formed, which may be further oxidized to benzhydrol or to the benzhydryl cation. In the other mechanisms, benzhydrol or one of its derivatives is formed directly.

It is repeatedly observed that steric effects are not important in this reaction. For example, cumene reacts faster than ethylbenzene, and the latter reacts faster than toluene. Similarly triphenylmethane reacts faster than diphenylmethane. Admittedly, this might result from a competition between a fundamental reactivity difference and a steric factor, but the universality of the observation with both aliphatic and aralkyl hydrocarbons suggest that this is not the case. On this basis, and remembering the very large steric effects associated with nucleophilic backside displacement reactions, it seems reasonable to exclude a backside electrophilic displacement as in mechanism E.

TABLE 11. RELATIVE RATES OF OXIDATION OF SOME COMPOUNDS IN 95% ACETIC ACID

Compound	Relative rate
Benzhydrol	30,000
Benzaldehyde	100
Fluorene	30
Anisole	3·4
Triphenylmethane	1·3
Diphenylmethane	1·00
Ethylbenzene	0·50
Toluene	0·16
Methylcyclohexane	0·08
t.-Amylbenzene	0·054
Neopentylbenzene	0·03
Cyclohexane	0·01

In mechanism C, the activated complex would of necessity be non-linear. An activated complex of this type would have three normal modes of vibration, one of which would degenerate into a translational mode.* Although this mode would no longer contribute a zero-point energy difference, the other two vibrational modes would still do so. The zero-point energy difference between activated complexes containing hydrogen and these containing deuterium would in part cancel the zero-point energy difference in the ground state resulting in a low kinetic isotope effect. Since the geometry and force constants for an activated complex of this type are difficult to estimate, we make use of the suggestion of Hawthorne and Lewis[27] that reactions of this type may be considered in a first approximation to involve the conversion of a bending mode in the ground state (rather than a stretching mode) to a translation in the activated complex. Making this assumption, and using a maximum value for the pre-exponential factor in the rate expression the maximum isotope effect would be estimated to be $k_H/k_D = 3{\cdot}6$. This is actually in very good agreement

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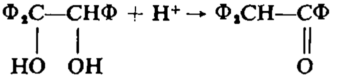
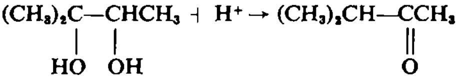
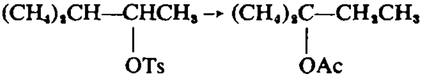
* It is probable that no one normal mode would correspond exactly to that required for leading to products. The argument still applies since one may translate the normal modes into the required ones.

[27] M. F. Hawthorne and E. S. Lewis, *J. Amer. Chem. Soc.* **80**, 4296 (1958).

with the results obtained in a number of hydrogen rearrangement reactions in which the activated complex must of necessity be non-linear (Table 12).

Since the observed kinetic isotope effect (6·4) is in the range of the maximum values which are experimentally observed, it would appear that mechanism C may be eliminated from consideration. Mechanism D may also fall in this category for the same reason, but because of the larger ring which is involved, there are as yet no good analogies. A better argument against mechanism D is that models suggest that considerable steric effects should be associated with the activated complex for this type of reaction. Again, since these appear to be absent, this mechanism is probably also incorrect.

TABLE 12. KINETIC ISOTOPE EFFECTS FOR HYDROGEN REARRANGEMENT REACTIONS

Reactions	k_H/k_D	Ref.
 $\underset{\text{HO}}{\Phi_2\text{C}}\text{—}\underset{\text{OH}}{\text{CH}\Phi} + \text{H}^+ \rightarrow \Phi_2\text{CH—}\underset{\text{O}}{\underset{\|}{\text{C}\Phi}}$	3·3	28
 $\underset{\text{HO}}{(\text{CH}_3)_2\text{C}}\text{—}\underset{\text{OH}}{\text{CHCH}_3} + \text{H}^+ \rightarrow (\text{CH}_3)_2\text{CH—}\underset{\text{O}}{\underset{\|}{\text{CCH}_3}}$	1·8	29
 $(\text{CH}_4)_2\text{CH—}\underset{\text{OTs}}{\underset{\|}{\text{CHCH}_3}} \rightarrow (\text{CH}_4)_2\underset{\text{OAc}}{\underset{\|}{\text{C}}}\text{—CH}_2\text{CH}_3$	2·1	30
ΦCHO† + $\text{HO}^- \rightarrow \Phi\text{CH}_2\text{OH} + \Phi\text{CO}_2^-$	1·8	31

† This assumes that the mechanism involves the addition of $\Phi\text{CH(OH)O}^-$ to ΦCHO followed by rate controlling intramolecular hydrogen migration.

This then leaves only mechanisms A and B to be considered. The effect of substituents may be used as an aid in differentiating between them. Mechanisms which involve the formation of an electron deficient carbon adjacent to an aromatic ring usually give a value of ρ^+ between -3 and -5.[24] For example, the solvolysis of benzhydryl chloride gave a ρ^+ of $-4·05$.[32] Hydrogen atom abstractions from toluene on the other hand normally give values of ρ between $-0·75$ and $-1·5$.[10] The value of ρ^+ obtained in the present reaction was $-1·17$, in good agreement with that for the latter type of reaction. It might be noted that in general hydrogen atom abstractions as well as reactions leading to carbonium ions are better correlated with σ^+ than with σ, and the reasons for this have been discussed by Russell.[33]

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[28] C. J. Collins, W. T. Rainey, W. B. Smith and I. A. Kaye, *J. Amer. Chem. Soc.* **81**, 460 (1959).

[29] W. B. Smith, R. E. Bowman and T. J. Kmet, *J. Amer. Chem. Soc.* **81**, 997 (1959).

[30] S. Winstein and J. Takahashi, *Tetrahedron* **2**, 316 (1958).

[31] K. B. Wiberg, *J. Amer. Chem. Soc.* **76**, 5371 (1954); C. G. Swain and W. A. Sheppard, *Abstract of papers presented at the 127th Nat. Meeting of the Amer. Chem. Soc., Cincinnati*, p. 40 N. American Chemical Society (1955).

[32] J. F. Norris and C. Banta, *J. Amer. Chem. Soc.* **50**, 1804 (1928); J. F. Norris and J. T. Blake, *Ibid.* **50**, 1808 (1928).

[33] G. A. Russell, *J. Org. Chem.* **23**, 1407 (1958).

Further evidence in support of mechanism A may be found in a comparison of the rates of hydrogen abstraction from toluene, ethylbenzene, diphenylmethane and triphenylmethane, and the rates of solvolysis of the corresponding chlorides (Table 13). It can be seen that there is good agreement between the rates of oxidation and the rates of hydrogen atom removal, but that the range of rates of solvolysis is larger by many orders of magnitude. It seems fairly clear then, that the initial reaction involves the abstraction on a hydrogen with one electron giving a benzhydryl radical as the first intermediate.

TABLE 13. RELATIVE RATES OF OXIDATION, HYDROGEN ABSTRACTION AND SOLVOLYSIS

Compound	Rel. rate of oxidation	Rel. rate[34] of H abst. by Cl_3C.	Rel. rate[35] of solvolysis of chlorides
Toluene	1·0	1·0	1·0
Ethylbenzene	3·1	3·0	100
Diphenylmethane	6·3	8·0	2000
Triphenylmethane	8·1	16·7	10^7

This is presumably the case with triphenylmethane and toluene also. It is interesting to note that a value of ρ^+ of $-1{\cdot}12$ may be calculated from the effect of substituents on the rate of oxidation of toluene.[14] This is very close to the value obtained in the present work.

There are several possible ways in which the benzhydryl radical may react further. First, there is a possibility of combination with the chromium(V) before the two species diffuse away from each other. Second, the radical may react with chromium (VI) either by an electron transfer process to give the benzhydryl cation and chromium (V), or by addition, giving an ester of chromium (V) which may decompose directly to benzophenone and chromium (III). It is not possible to distinguish between these possibilities by simple kinetic experiments alone. Therefore a detailed discussion of this feature of the reaction will be postponed until further experimental work has been completed.

The unusual reactivity of the *p*-methoxy substituted compounds must now be considered. The data which are available exclude a chain process. Thus one is led to the conclusion that the reaction which occurs in this case is probably one in which greater electron deficiency is found at the site of the reaction than with the other diphenylmethane derivatives. The *p*-methoxy group is unusually well able to stabilize an electron deficiency.[36] The data also support the assumption of a change in mechanism for the reaction of this compound. For example, the effect of water concentration in the solvent, and the value of the entropy of activation were markedly different than for diphenylmethane. One of the simplest rationalizations is that the process involves hydride abstraction with the methoxy substituted derivative, leading to the benzhydryl cation. However, it is difficult to present definitive evidence for any particular mechanism based on the little data which are now available.

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[34] E. C. Kooyman, *Rec. Trav. Chim.* **69**, 492 (1950).
[35] A. Streitwieser, Jr., *Chem. Rev.* **56**, 571 (1956).
[36] N. C. Deno and A. Schriesheim, *J. Amer. Chem. Soc.* **77**, 3051 (1955).

It might be noted that there are several examples of reactions in which the introduction of a *p*-methoxy group caused the mechanism to change from a free radical type to one involving a carbonium ion. For example, Criegee *et al.*[37] examined the reaction of styrene and *p*-methoxystyrene with lead tetrabenzoate in benzene solution. The former gave the normal product of a free radical type reaction, phenyl-1, 2-ethanediol benzoate, whereas the latter gave a product, 2-*p*-methoxyphenyl-1, ethanediol dibenzoate, which almost certainly arose via the formation of a cationic species.

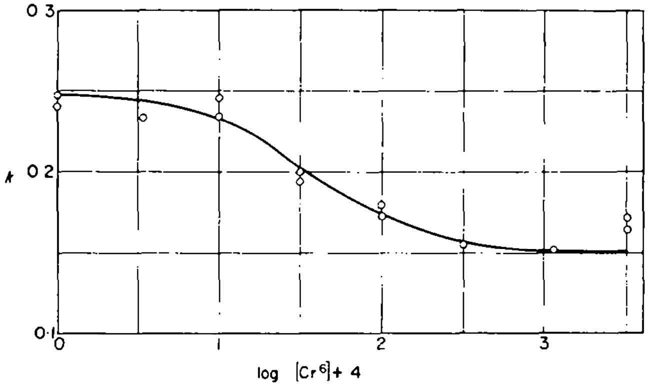

FIG. 6. Effect of chromium (VI) concentration on the rate of oxidation of di-isopropyl ether. The data are taken from ref. 6.

Finally, there are two aspects of the reaction which deserve special comment. These are the kinetic dependence on total chromium (VI) concentration, and the effect of the water concentration of the solvent on the rate of reaction. As was mentioned previously, the oxidations of alcohols and of aldehydes, both of which are believed to proceed via an ester mechanism, have a kinetic dependence on only the acid chromate ion, whereas in the present case, it is apparent that both the acid chromate ion and the dichromate ion must be reactive. The latter is also true for the oxidation of methylcyclohexane,[16] and of diisopropyl ether[6] (Fig. 6). In the latter three cases hydrogen abstraction must occur directly by means of the oxidizing agent. However, in the reactions of aldehydes and of alcohols, a likely path for the formation of the intermediate ester is

$$\mathrm{ROH} + \mathrm{HCr_2O_7^-} \longrightarrow \mathrm{ROCrO_3^-} + \mathrm{HCrO_4^-} + \mathrm{H^+}$$

Thus the rate law for the overall reaction would be

$$v = \frac{k[\mathrm{ROH}][\mathrm{Cr_2O_7^=}][\mathrm{H^+}]}{[\mathrm{HCrO_4^-}]} = k'[\mathrm{ROH}][\mathrm{HCrO_4^-}][\mathrm{H^+}]$$

The formation of the ester may then actually involve the dichromate ion, resulting in a kinetic dependence on only the acid chromate ion. It is proposed that this difference in rate law between the two types of reactions may serve to differentiate between the reactions involving an ester intermediate, and those involving direct hydrogen abstraction.

It has also been noted that the rates of oxidation of hydrocarbons and of alcohols

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[37] R. Criegee, P. Dimroth, K. Noll, R. Simon and C. Weis, *Chem. Ber.* **90**, 1070 (1957).

by chromic acid are strongly accelerated by decreasing the water content of the medium,[2,16] whereas, at a constant value of the acidity function, H_0, the rate of oxidation of benzaldehyde was unaffected by the water content.[8] The data which are presently available are not sufficiently complete to make a detailed analysis, but at a constant value of H_0, it appears that the oxidation of alcohols and of hydrocarbons is subject to an approximate first order retardation by water. The reason for this is not difficult to see. The H_0 acidity function is defined for the reaction

$$H^+ + B \rightleftharpoons BH^+$$

whereas the reaction in question is of the type

$$H^+ + A^- \rightleftharpoons HA$$

which requires the acidity function H_-. Unfortunately, values for this acidity function in the medium used are not available, but an estimate of the difference between H_0 and H_- may be made. We have previously noted that a plot of $H_0 - \log [H^+]$ against $\log M_{H_2O}$ for dilute perchloric acid solutions in aqueous acetic acid mixtures gave a straight line from 25–95 per cent acetic acid, having a slope of 2.[20] Since the net charge is not changed in the reaction, this slope may be roughly equated with the change in the number of water of hydration in the reaction

$$H^+ \cdot nH_2O + B \rightleftharpoons BH^+ \cdot (n-2)H_2O + 2H_2O$$

In the reaction of an anion with a solvated proton, a larger number of water molecules of hydration will be liberated, since the conjugate acid, HA, will be relatively non-solvated. If the number of water of hydration of BH^+ in these solutions is one (i.e. n above equals 3) then the difference between H_0 and H_- will be roughly $\log M_{H_2O}$ (remembering however, that H_- will be more strongly affected by a change in dielectric constant than will H_0). Thus in the absence of other better data, it is suggested that the effect of water on the rate of oxidation of alcohols and of hydrocarbons may be used as a rough measure of the change in H_- with water concentration.

These suggestions are in good accord with the data we have obtained on the oxidation of benzaldehyde with chromic acid. It was assumed that a water molecule is required for the abstraction of a proton from the intermediate ester. Here, the rate expression will contain the concentration of water, and instead of obtaining first order retardation by water, the latter now has no effect. This illustrates the use of this rough H_- scale to determine the number of water molecules associated with the activated complex. In connection with the alcohol oxidation it must be remembered that although a water molecule is required for the decomposition of the intermediate ester, one water molecule is formed in the prior equilibrium, and so the net number of water molecules involved is zero.

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