

337. *A Study of the Mechanism of Oxidation with Chromic Acid. Part II.*

By RONALD SLACK and WILLIAM A. WATERS.

The rates of oxidation of diphenylmethane and of related hydrocarbons with chromium trioxide in glacial acetic acid solution are extremely rapid at first, but soon slacken and stop almost entirely after a few hours though both hydrocarbon and Cr^{VI} remain in the solution. Benzyl radicals may be concerned in the reaction but must be destroyed rapidly by the oxidising agent.

The cessation of the reaction is brought about by Cr^{III} which removes CrO₃ as the inert CrO₄⁻ or Cr₂O₇⁻ anions. Other kations and water exert the same effect, whilst the addition of 2.5% of sulphuric acid results in rapid and complete oxidation even at room temperature.

A SURVEY of attempts to elucidate the mechanism of oxidation of organic compounds by chromium trioxide shows that a general correlation cannot easily be made. Many substances are smoothly and completely oxidised in aqueous solution, but unfortunately, special postulates have often been necessary to explain the idiosyncrasies of individual compounds of the same class. Thus, Sneath (*Rec. Trav. chim.*, 1940, **59**, 111; 1941, **60**, 199; 1942, **61**, 213) found that, whereas the rates of oxidation of succinic acid and formic acid depended largely on the proportion of mineral acid added, no proportionality could be observed with malonic acid. Similarly, although a bimolecular equation gave fairly good constants for succinic acid, the oxidation of oxalic and adipic acids could not be so expressed. Again, Lucci (*Boll. sci. Fac. Chim. Bologna*, 1940, **1**, 333; 1941, **2**, 165, 176) has shown that many aromatic aldehydes gave second-order constants on oxidation, but the data for the three hydroxybenzaldehydes were represented by first-order equations. Westheimer and Novick's equation (*J. Chem. Physics*, 1943, **11**, 506) for the oxidation of isopropanol affords yet a further variety.

In a preliminary survey (Part I) it was suggested by one of us (Waters, *J.*, 1946, 1151) that

the initial attack of chromium trioxide on an organic compound was neutral hydrogen abstraction, and it seemed possible that a rationalisation of the kinetic results might emerge on this basis. Experiments have therefore been made with various aromatic hydrocarbons, particularly diphenylmethane which oxidises at a convenient rate for study. Glacial acetic acid was used as a solvent since it is almost inert under the conditions of reaction and gives homogeneous solutions. The course of all the oxidations was followed iodometrically. The sparing solubility (about 1%) of chromium trioxide in acetic acid limits the range of concentrations and an added complication may arise from the formation of chromoacetic anhydride or its acetate (Pictet and Genequand, *Ber.*, 1903, **36**, 2216).

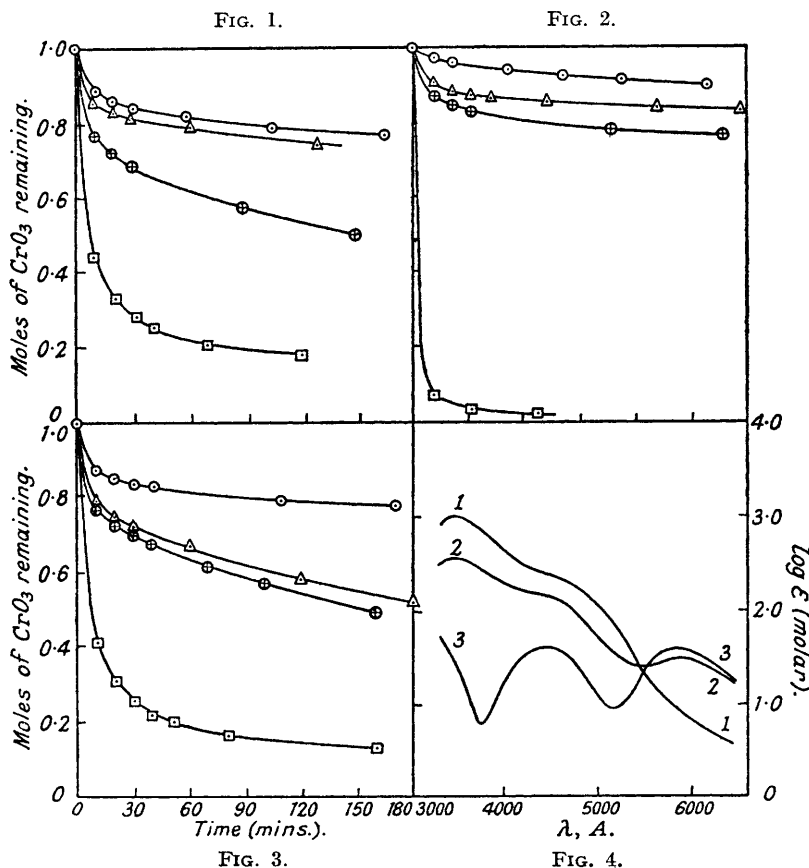


FIG. 1.
 ○ 18°
 △ 23°
 ⊕ 40°
 □ 40° Excess diphenylmethane.
 1 : $\frac{3}{2}$, CrO₃ : diphenylmethane.

FIG. 3.
 ○ Benzhydryl acetate.
 △ Tetraphenylethane.
 ⊕ Diphenylmethane.
 □ Benzhydrol.
 Constant CrO₃. Oxidant stoichiometric for benzophenone production. Temp. = 18°.

FIG. 2.
 ○ 2 : 1, CrO₃ : toluene.
 △ 1 : 3, CrO₃ : diphenylmethane.
 ⊕ 1 : 3, CrO₃ : triphenylmethane.
 □ 1 : $\frac{3}{2}$, CrO₃ : fluorene.
 Temp. = 30°.
 FIG. 4.
 (1) CrO₃ in acetic acid.
 (2) Final reaction mixture; 1 : $\frac{3}{2}$, CrO₃ : diphenylmethane.
 (3) Fully reduced CrO₃ in acetic acid.

Fig. 1 illustrates the general course of the oxidation of diphenylmethane. Characteristic features of the reaction are : (1) The extraordinarily fast initial rate, which varies in extent with the varying concentrations of the reactants and with temperature. (2) The noticeable decrease in the reaction rate, which finally leads to almost complete cessation of the reaction. (3) The

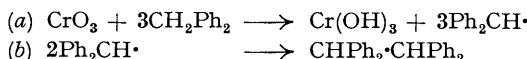
relatively small effect of temperature. The percentage of oxidising agent finally remaining is approximately constant and does not, within certain limits, depend on the hydrocarbon-CrO₃ ratio (see below—results at 18°):

Molar proportion.		Residual CrO ₃ , %. (72 hrs.).	Molar proportion.		Residual CrO ₃ , %. (72 hrs.).
CH ₂ Ph ₂ .	CrO ₃ .		CH ₂ Ph ₂ .	CrO ₃ .	
4	4	17	4	2	15
4	3	15	4	1	14.5

Fig. 2 shows the variation in extent of oxidation, different hydrocarbons being used under standard conditions. Whereas difficultly oxidised compounds, *e.g.*, toluene, diphenylmethane, and triphenylmethane, did not reduce all the chromium trioxide in 1–3 days, easily oxidised hydrocarbons, *e.g.*, fluorene, phenanthrene, acenaphthene, and indene, reduced it completely.

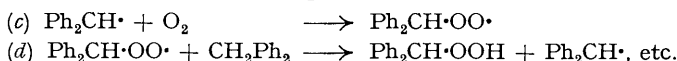
The oxidation of diphenylmethane yields mainly benzophenone. No benzhydrol or benzhydryl acetate has been isolated but small amounts of *s*-tetraphenylethane are always found, even during the initial stages. Subsequently, some slight attack at a Ph-C bond takes place and traces of benzoic acid and of phenolic products have been found. We also obtained evidence of the formation of a little succinic acid. Triphenylmethane behaves in a parallel manner and benzophenone and phenol are produced in small yield, the main product in this case being triphenylcarbinol.

A comparison of the rates of oxidation of diphenylmethane, benzhydrol, benzhydryl acetate, and *s*-tetraphenylethane (Fig. 3) reveals that the acetate cannot, in fact, be formed during oxidation since it would accumulate amongst the products. The rate of oxidation of tetraphenylethane is similar initially to that of diphenylmethane, but the ultimate divergence indicates that a steady build-up should occur if (a) followed by (b) both comprise main steps in the formation of benzophenone:

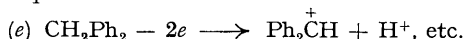


The small yield of tetraphenylethane indicates that (b) at least is a side reaction. However, the production of this hydrocarbon provides good support for the dehydrogenation theory (Part I), particularly since it has been shown by Nauta and Mulden (*Rec. Trav. chim.*, 1939, 58, 1070) that dimerisation of the diphenylmethyl radical is one of its characteristic reactions in solution. Again, the detection of succinic acid, evidently an oxidation product of the solvent, supports the free-radical theory (cf. Kharasch *et al.*, *J. Amer. Chem. Soc.*, 1943, 65, 15; *J. Org. Chem.*, 1945, 10, 394).

Organic peroxide formation (cf. Part I) has been excluded except as a minor side-reaction, for the comparative rates of oxidation of diphenylmethane in air and in carbon dioxide show only insignificant differences. Hence the sequence



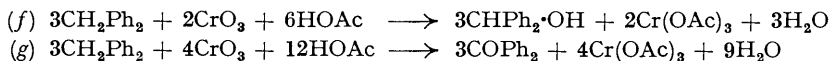
must be much slower reactions than that of Ph₂CH⁺ with CrO₃. The participation of the kation Ph₂CH⁺, *e.g.*, via the ionic sequence



is unlikely since this would yield the stable ester CHPh₂·OAc which could not be detected

A sequence more or less analogous with that suggested for the course of the Etard reaction (Rohde, *Sammlung chem. u. chem. tech. Vorträge*, 1901), involving organic chromium complexes containing Cr^V or Cr^{IV}, does not seem improbable. However, we have found no evidence of the existence of intermediate valency states. These would be expected to have characteristic absorption spectra and our final mixtures disclose only the presence of Cr^{VI} and Cr^{III} (Fig. 4), but these results do not preclude the possibility of disproportionation of Cr^V or Cr^{IV} *in situ*. The relative amounts of Cr^{VI} and Cr^{III} determined from Fig. 4 agree well with the iodometric estimations and with gravimetric estimations of Cr^{VI} as lead chromate.

The Significance of the Chromium Trioxide–Chromic Acid Equilibrium.—The introduction of benzophenone or of a small amount of tetraphenylethane has no pronounced effect on the velocity of oxidation of diphenylmethane, nor is the presence of a *small* amount of water, corresponding to the overall stoichiometry



deleterious. However, addition of the Cr^{III} ion or of anything which serves to convert the oxidising agent in sufficient quantity into $\text{CrO}_4^{=}$ (or HCrO_4^-) or $\text{Cr}_2\text{O}_7^{=}$ ions has a very marked inhibitory effect. This phenomenon offers an attractive explanation of the inhibited reactions, for the effective removal of active chromium trioxide, as chromic chromate or dichromate would produce such an effect. This hypothesis receives support from the fact that replacement of the original trioxide by an equivalent amount of either potassium chromate or dichromate virtually eliminates all oxidation under the standard conditions (Fig. 5a). Any kation can effect this

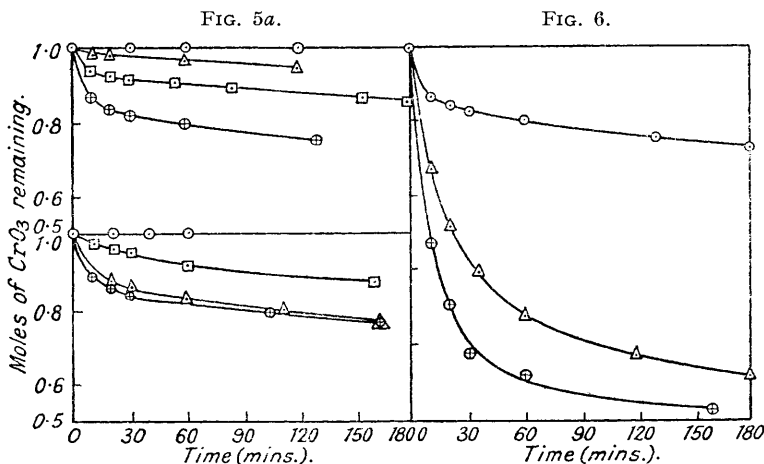


FIG. 5a.

- Chromate or dichromate.
- △ Cr^{III} addition (2 molar proportions).
- ◻ Cr^{III} addition (1 molar proportion).
- ⊕ 1 : 3, CrO_3 : diphenylmethane (control).

FIG. 5b.

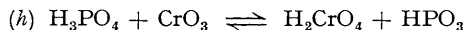
- 5% water = 0.56 g.-molar.
- ◻ 2.5% water = 0.28 g.-molar.
- △ 1.25% water = 0.14 g.-molar.
- ⊕ 1 : 3, CrO_3 : diphenylmethane (control).

Concentration CrO_3 = 0.005 g.-molar. Temp. = 18°.

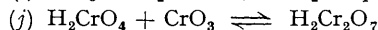
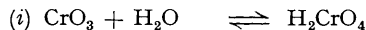
FIG. 6.

- 1 : 3, CrO_3 : diphenylmethane (control).
 - △ with H_2SO_4 : $2\text{H}_2\text{O}$.
 - ⊕ with H_2SO_4 : H_2O .
- Temp. = 23°.

change. Thus the addition of anhydrous potassium acetate completely inhibits reaction. Similarly, the addition of substances capable of fairly easy dehydration, *e.g.*, orthophosphoric acid, produces identical results. Some slight ultimate attack in the latter case is presumably a measure of the equilibrium



The change in colour which occurs in an acetic acid solution of chromium trioxide on the addition of any of the above substances is characteristic of the formation of chromate or dichromate; the original opaque dark-red solution at once becomes a transparent orange-yellow. This same colour change, accompanied by a corresponding loss in power of oxidation, is produced by the addition of varying amounts of water, though Fig. 5b shows that the equilibria



are decidedly in favour of the dehydrated agent.

Elimination of both the kation and the water effects can be accomplished by the addition of concentrated sulphuric acid to the reaction mixture, and it can be seen from the following table

H_2SO_4 , %.	Residual CrO_3 , as c.c. of N/10-thiosulphate, after 10 mins.	H_2SO_4 , %.	Residual CrO_3 , as c.c. of N/10-thiosulphate, after 10 mins.
0	12.4	5.0	0
1.25	7.3	10.0	0
2.5	0.2		

that rapid and complete oxidation occurs in the presence of only 2.5% (by volume). It is significant that chromic sulphate is invariably deposited from the reaction mixture in the illustrative cases. Under these conditions, estimation shows that more than 80% of the hydrocarbon is rapidly converted into ketone despite the fact that some oxidation of the solvent occurs. At low temperatures this side reaction is insignificant, but rapid disruptive oxidation occurs at 100°. Fig. 6 shows clearly that the sulphuric acid and water effects are competitive, though the use of a reagent corresponding to sulphuric acid monohydrate (84% w/w) allows tolerably fast reaction.

Elimination of the water effect can also be achieved in part by the use of an acetic acid-anhydride mixture, but this leads to other peculiarities. Eventually, however, the usual inhibition manifests itself and the reaction does not go to completion. In the presence of acetic anhydride, hot solutions of chromium trioxide in acetic acid are partly reduced, and the formation of succinic acid can clearly be demonstrated.

The investigation is being continued and a more detailed examination of the kinetic problems will be reported.

EXPERIMENTAL.

Materials.—Glacial acetic acid was stabilised by two successive distillations from chromium trioxide; large head and tail fractions were rejected, and acid boiling over a 1° range only was collected for use. All hydrocarbons were distilled or crystallised at least twice. Chromium trioxide was "AnalaR" material dried in a vacuum over sulphuric acid; all other inorganic reagents were of "AnalaR" quality.

Reaction-velocity Measurements.—Accurately prepared w/v solutions of chromium trioxide and of hydrocarbon in acetic acid were allowed to reach the required temperature in a thermostat, and aliquots were then mixed as rapidly as possible. Samples, withdrawn at known time intervals, were quenched in a standard, previously prepared mixture of potassium iodide and dilute sulphuric acid, and the residual chromium trioxide was estimated iodometrically. To minimise thermal inaccuracies at temperatures greater than 30°, all pipettes were kept within the thermostat.

Investigation of Reaction Products.—(a) *Diphenylmethane.* The reactants mixed as above in several different stoichiometrical proportions were kept for 24 hrs. at constant temperature. The mixtures were then quenched in acid ferrous sulphate solution and extracted repeatedly with ether. The ethereal extracts were washed with water and all the acidic components were removed by sodium hydroxide extraction. It was found empirically that most of the acetic acid was removed in the first few colourless washings, the acidic oxidation products appearing only in the later, markedly coloured washings. After being dried (Na₂SO₄), the ethereal layer was carefully fractionated, finally under reduced pressure, and gave only diphenylmethane and benzophenone. The bath temperature was never allowed to exceed 190°. The portion which did not distil gave colourless crystals, m. p. 209–210°. Recrystallisation from ligroin raised the m. p. to 211° and this was unchanged by admixture with authentic *s*-tetraphenylethane (Norris *et al.*, *Ber.*, 1910, **43**, 2959). The alkaline extracts were acidified with sulphuric acid, extracted with ether, and divided, by successive sodium hydrogen carbonate and hydroxide washes, into acidic and phenolic portions. After acidification, the former was re-extracted with ether, and the extract evaporated to dryness. The residue was dissolved in boiling ligroin, filtered (charcoal), and allowed to crystallise. This product was sublimed at 100°/5 mm., and the sublimate on crystallisation from water gave white plates, m. p. 119–120°, undepressed by admixture with authentic benzoic acid.

Only traces of phenolic material were obtained from the sodium hydroxide extracts, but the colour produced on coupling with diazotised *p*-nitroaniline was indistinguishable from that of phenol itself when parallel conditions were used. Variations in reaction temperature had no effect on the qualitative results: a slight increase in the yield of acid and phenolic material was observed at 100°. The maximum yield of tetraphenylethane was only of the order of 2%, and that of the other by-products was considerably less than this. A positive colour reaction which indicated the presence of succinic acid was also obtained (see below).

(b) *Triphenylmethane.* The hydrocarbon (22.0 g.) and 1% chromium trioxide solution in acetic acid (300 c.c.) were kept at 30° for 16 hrs. Phenolic, acidic, and neutral fractions were obtained as described above. Triphenylmethane and triphenylcarbinol, m. p. 160–162°, were obtained from the last by fractional crystallisation from alcohol, the final liquors being distilled in a bulb-tube under reduced pressure. Treatment of the distillate with 2:4-dinitrophenylhydrazine sulphate in methanol gave orange benzophenone 2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 231–232°.

No acidic material was found; traces of crude phenolic material gave, on bromination in aqueous solution, colourless needles, which, crystallised from alcohol, had m. p. 89°. Authentic 2:4:6-tribromophenol, m. p. 92°, showed no depression on admixture.

Oxidation of Acetic Acid.—A mixture of acetic acid (200 c.c.), acetic anhydride (100 c.c.), and chromium trioxide (50 g.) was heated on the steam-bath until the vigorous, almost uncontrollable reaction had ceased. The initial reaction (at *ca.* 90°) required considerable cooling. When reaction had subsided the bulk of the solvents was removed in a vacuum and the residue treated in a number of ways:

(a) The chromium was precipitated from its aqueous acetate solution with dilute ammonia, and the filtrate concentrated after acidifying with hydrochloric acid. A little alcohol was added during this process to destroy unchanged Cr^{VI}. The concentrate was again made alkaline, boiled, filtered, and evaporated. The residual salts gave a strongly positive sulphuric-resorcinol reaction indicative of succinic acid.

(b) The aqueous solution of chromic acetate was partly neutralised with ammonia and treated with excess of barium chloride. The resulting precipitate, which contained barium chromate, was warmed with sodium carbonate solution, filtered, and reduced with hydrochloric acid and sodium sulphite. The

solution was made alkaline and filtered, and the filtrate evaporated to dryness. The residue again gave a positive test for succinic acid.

(c) Attempted esterification of residual organic acids produced no product which could be identified as ethyl succinate.

More unambiguous results were obtained by the oxidation of acetic acid with chromium trioxide in glacial acetic and sulphuric acids at fairly low temperatures (*ca.* 20°). Much carbon dioxide was evolved throughout, but after dilution with water, continuous ether extraction, removal of the ether, treatment of the residue with ammonia, evaporation to dryness, and distillation with zinc dust the characteristic smell of pyrrole was observed. Its identity was confirmed by means of strongly positive pine-splint tests.

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DYSON PERRINS LABORATORY, OXFORD.

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