128. *A Study of the Mechanism of Oxidation with Chromic Acid. Part IV. Kinetics of the Initial Reaction.*

By R. SLACK and WILLIAM A. WATERS.

The initial reaction between chromium trioxide and diphenylmethane in glacial acetic acid solution is of second order with respect to the chromium trioxide and of first order with respect to the hydrocarbon. With triphenylmethane the reaction is of first order with respect to chromium trioxide. In the initial reaction four equivalents of Cr^{VI} are locked up for each one which is irretrievably reduced to Cr^{III}.

It is suggested that chromic acid oxidation of hydrocarbons proceeds in stages and involves the formation of transient complexes of Cr^{VI} and Cr^{IV} analogous to those concerned in chromyl chloride oxidations (Étard's reaction).

One of the final reaction products is a stable chromium acetochromate, $Cr^{III}(HCrO_4)(O{\cdot}CO{\cdot}CH_3)_2$.

PART II of this series (*J.*, 1948, 1666) showed that the oxidation of hydrocarbons, such as diphenylmethane, by chromium trioxide in glacial acetic acid solution commenced very rapidly but soon slackened off, and finally ceased before all the Cr^{VI} had been reduced to Cr^{III}; further, it was established that chromic kations inhibited reaction by leading to the stabilisation of relatively inert chromate $(CrO_4)^{=}$ or dichromate $(Cr_2O_7)^{=}$ anions in the solution. We have now followed up this work in two ways: (*a*) by isolating a complex *chromium acetochromate* from reaction mixtures, and (*b*) by studying more minutely the initial stages of the oxidation process. The latter approach has given further insight into the mechanism of chromium trioxide oxidation and of its relationship to oxidation by chromyl chloride (Étard's reaction).

When a concentrated solution of chromium trioxide in cold acetic anhydride is treated with a solution of an oxidisable organic compound, such as diphenylmethane, triphenylmethane, or hydrobenzoin in cold glacial acetic acid, a greenish-brown powder is soon precipitated. Samples of this have been separated and analysed for (i) total chromium content, (ii) sexavalent chromium, and (iii) acetic acid. In every case, the product gives an analysis corresponding fairly closely with that for a chromium acetochromate of formula $Cr^{III}(HCrO_4)(OAc)_2$, containing equimolar proportions of Cr^{III} and Cr^{VI}. The action of iodine on chromium trioxide in glacial acetic acid produces a similar sparingly soluble salt, of composition approximating to the *acetoiodate*, $Cr^{III}(IO_3)(OAc)_2$.

The production of this sparingly-soluble chromic acetochromate at even an early stage in the oxidations of organic substances appeared to indicate that the amount of titratable Cr^{VI} rendered inert by the oxidation of diphenylmethane and its analogues might be *twice* the decrease in Cr^{VI} titre according to estimations carried out by the standard routine of quenching the oxidising mixture in aqueous potassium iodide and then determining free iodine with sodium thiosulphate. Consequently, kinetic studies of the oxidation of diphenylmethane by chromium trioxide were re-examined on the basis that

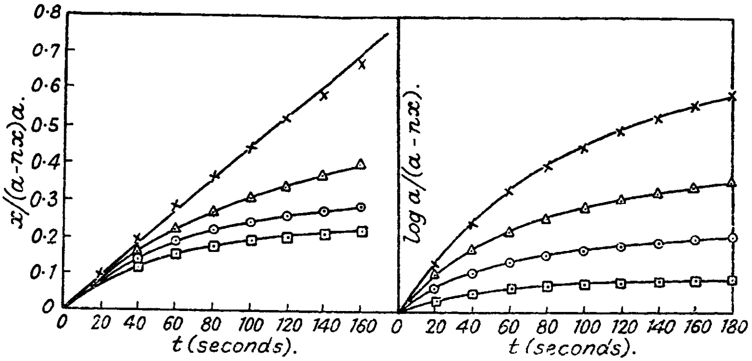
Cr^{VI} remaining at time $t = (a - 2x)$, where a = initial titre and $(a - x)$ = titre at time t.

Since in many oxidations more than half the initial Cr^{VI} is completely reduced to Cr^{III} in less than 10 minutes, it was necessary to modify the experimental technique, and to conduct measurements at time intervals of integral multiples of 10 seconds. Plots of the initial rate of oxidation showed that the reaction velocity had decreased very considerably from its initial value when only 10% of the Cr^{VI} had been reduced to Cr^{III}, and even when the hydrocarbon was present in large excess (10—20 moles) it was quite impossible to represent the results by an equation of the type $-\,d[CrO_3]/dt = k(a - 2x)^n$.

Though we envisaged (compare Part II) that even initially all the chromium trioxide might not be present in the active state, and feared that it might be erroneous to assume that at $t = 0$, a = total Cr^{VI} in solution, we decided to test the validity of equations of the general type $dx/dt = k(a - nx)^m$, where a = initial Cr^{VI}; x = titre decrease at time t, and n and m are integers.

Fig. 1 shows that when $n = 4$ the above equation gives a nearly linear plot for the integrated expression $kt = x/(a - nx)a$ for a second-order reaction ($m = 2$), and Fig. 2 shows that no such result can be achieved for the expression $kt = (1/n) \log a/(a - nx)$. Hence we conclude that the *initial* stage of the oxidation of diphenylmethane by chromium trioxide is *of second order with respect to " active chromium trioxide,"* and that *four* equivalents of Cr^{VI} are put out of action for each equivalent of Cr^{VI} which is irretrievably reduced to Cr^{III} on treatment of the reaction mixture with water.

FIG. 1. FIG. 2.



Figs. 1 *and* 2. *The initial reaction at* 18° : *diphenylmethane in large excess.*
Initial concn. of CrO_3 = 0·009734 *g.-mol./l.*
Initial concn. of CH_2Ph_2 = 0·1180 *g.-mol./l.*
×, $n = 4$. △, $n = 3$. ⊙, $n = 2$. □, $n = 1$.
x has been expressed as a fraction of a.

Now the stoicheiometrical equation $4CrO_3 + 3CH_2Ph_2 + 12HOAc = 3COPh_2 + 4Cr(OAc)_3 + 9H_2O$ would indicate that $\frac{3}{4}$ of a mole of diphenylmethane should be oxidised per mole of chromium trioxide reduced, and consequently a kinetic expression which is *of first order with respect to the hydrocarbon* should be of the form (A)

$$\text{(A)}\quad dx/dt = k(a - 4x)^2(b - \tfrac{3}{4}x)$$

to agree with our previous conclusions concerning the consumption of " active chromium trioxide." The integrated form of (A) is (B)

$$\text{(B)}\quad kt = \frac{4}{a(4b - \frac{3}{4}a)} \cdot \frac{x}{(a - 4x)} + \frac{\frac{3}{4}}{(\frac{3}{4}a - 4b)^2} \cdot \log \frac{b(a - 4x)}{a(b - \frac{3}{4}x)}$$

where the second term is significant only when b (the initial concentration of the hydrocarbon) is not much greater than a. This expression was found to fit the initial stages of diphenylmethane oxidation quite well up to the time at which x approaches $0{\cdot}2a$.

Fig. 3 illustrates the correspondence between observed and calculated reaction velocities for the initial periods of the oxidation, whilst Fig. 4 shows that at high dilution expression (*B*) can hold for the first hour of an oxidation. Table I, giving the correspondence between

TABLE I.

Initial velocity constants for oxidation of diphenylmethane with chromium trioxide at **18°.**

Initial concns. (g.-mol./l.).		*k* (sec.$^{-1}$),	
CrO_3.	CH_2Ph_2.	neglecting log term.	including log term.
[0·009734	0·0145	1·56	1·39]
0·009734	0·0290	5·60	5·49
0·009734	0·0594	5·52	5·39
0·009734	0·1180	4·34	4·34
0·009734	0·00973	9·21	7·56

calculated values of *k* for different hydrocarbon concentrations, demonstrates the validity of the assumption that the oxidation of diphenylmethane is approximately of first order with respect to the hydrocarbon

FIG. 3.

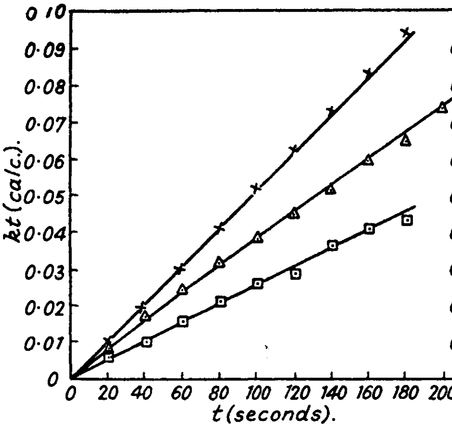


Fig. 3. *Equation* (*B*) *applied to the initial rate at* 18°.

Graph ×.

Initial concn. of CrO_3 = 0·01847 *g.-mol./l.*
Initial concn. of CH_2Ph_2 = 0·0145 *g.-mol./l.*

Graph △.

Initial concn. of CrO_3 = 0·009734 *g.-mol./l.*
Initial concn. of CH_2Ph_2 = 0·0290 *g.-mol./l.*

Graph □.

Initial concn. of CrO_3 = 0·009734 *g.-mol./l.*
Initial concn. of CH_2Ph_2 = 0·0594 *g.-mol./l.*
(*log term neglected since* $a \gg b$.)

In all cases the value of a *has been normalised.*

FIG. 4.

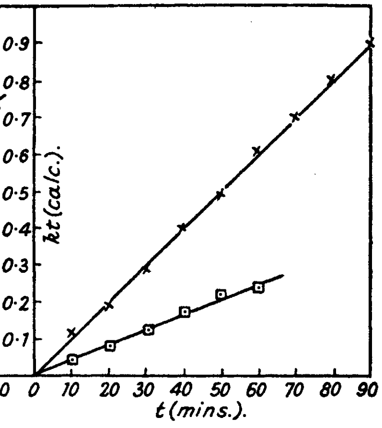


Fig. 4. *Equation* (*B*) *applied to the reaction at* 30·5°.

Graph ×.

Initial concn. of CrO_3 = 0·010 *g.-mol./l.*
Initial concn. of CH_2Ph_2 = 0·0075 *g.-mol./l.*

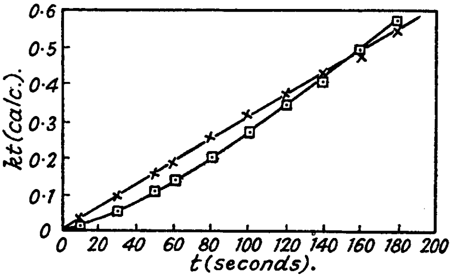
Graph □.

Initial concn. of CrO_3 = 0·020 *g.-mol./l.*
Initial concn. of CH_2Ph_2 = 0·0150 *g.-mol./l.*

The kinetic expression (*A*) can, at most, give us no more than a clue to the first stage of a complex sequence of reactions. It indicates, however, that, whatever may be the way in which the Cr^{VI} is eventually reduced, there first occurs a rate-determining reaction between one molecule of hydrocarbon and two molecules of chromium trioxide. Now it is significant that Étard (*Ann. Chim. Phys.*, 1881, **22**, 218) has shown that the oxidations of hydrocarbons RCH_3 or $R''CH_2$ by chromyl chloride in carbon disulphide solution proceed by way of the formation of a complex of formula $R''CH_2,2CrO_2Cl_2$ which breaks down on the addition of water. We therefore suggest that the oxidation of diphenylmethane by chromium trioxide probably proceeds by way of the formation of a complex, $CH_2Ph_2,2CrO_3$, of similar structural type.

Since we had previously (*loc. cit.*) found no evidence for even the transient production of benzhydrol, or its acetate, from diphenylmethane, we concluded that in the complex, $CH_2Ph_2,2CrO_3$, one chromium atom had become associated with each oxidisable C–H link. It was therefore of interest to compare the oxidation of diphenylmethane with that of triphenylmethane. Though the prolonged oxidation of these two hydrocarbons pursues a very similar course, their initial stages are markedly different, and Fig. 5, which gives the results obtained for an oxidation carried out in the presence of a large excess of hydrocarbon, indicates that the appropriate kinetic expression is now

FIG. 5.



Oxidation of triphenylmethane at 24°.

Initial concn. of CrO_3 = 0·010 *g.-mol./l. Very large excess of triphenylmethane.*

Graph ×. *First order relationship*: $kt \propto \log 1/1 - 4x)$.

Graph ⊡. *Second order relationship*: $kt \propto x/(1 - 4x)$.

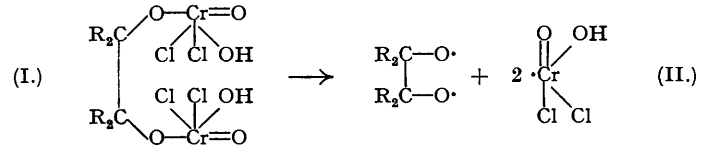
$$\text{(C)}\quad dx/dt = k(a - 4x)$$

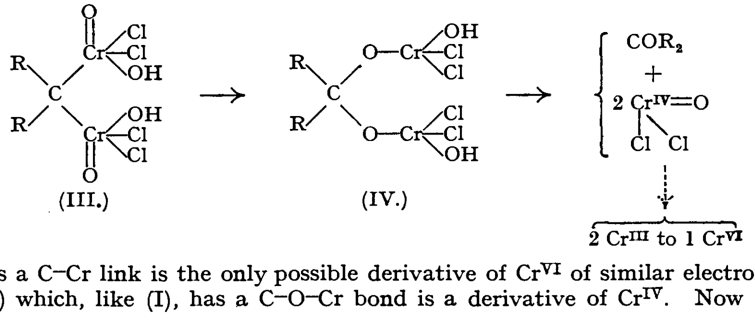
which is of *first order* with respect to the chromium trioxide.

This would correspond to the formation of a complex of structure $CHPh_3,CrO_3$. In support of this hypothesis we have made and analysed the Étard *complex* of triphenylmethane (compare Perkin and Law, *J.*, 1908, **93**, 1634) and have found it to be $CHPh_3,CrO_2Cl_2$.

DISCUSSION.

Étard (*loc. cit.*) showed that complex formation between oxidisable hydrocarbons and chromyl chloride occurred without loss of either hydrogen chloride or water, and noted that when his complexes were subsequently decomposed by water some Cr^{VI} was set free. In Part III (preceding paper) we described the formation and breakdown of very similar complexes which may be formed by the action of chromyl chloride on 1 : 2-glycols, and assigned to them structures containing Cr^{VI} of type (I) which we suggested might break down homolytically to oxygen diradicals and a transient derivative of Cr^{V}. Now a Cr^{VI} complex with a C—O—Cr bond structure cannot be written for a hydrocarbon–chromyl chloride adduct;



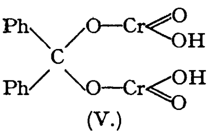


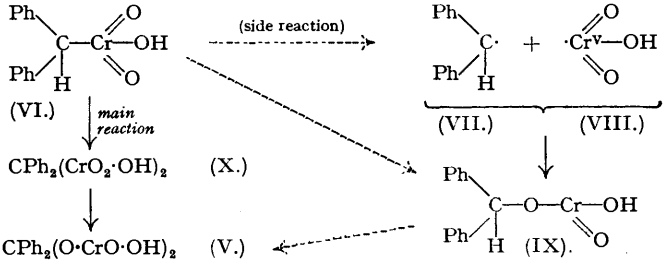
(III) which has a C–Cr link is the only possible derivative of Cr^{VI} of similar electronic type to (I), whilst (IV) which, like (I), has a C–O–Cr bond is a derivative of Cr^{IV}. Now (IV) would be expected to break down with water to a ketone and a mixture of both Cr^{III} and Cr^{VI}; such a fission would correspond very closely to the *final* course of the Étard reaction, which can convert hydrocarbons CH$_2$R$_2$ into ketones COR$_2$, and triphenylmethane into triphenylcarbinol in almost quantitative yield. We would therefore suggest that the Étard reaction, and probably the chromic acid oxidation of hydrocarbons, does at some stage pass through a complex of type (IV), but that (III) is the more likely *initial* product. In this connection it may be noted that definite evidence for the real existence of a complex of type (III) can be adduced from the fact that the addition complex of *o*-nitrotoluene and chromyl chloride decomposes on treatment with water according to the scheme

$$o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3,2\text{CrO}_2\text{Cl}_2 + 2\text{H}_2\text{O} = o\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_3 + 2\text{CrO}_3 + 4\text{HCl}$$

(von Richter, *Ber.*, 1886, **19**, 224; Stuart and Elliot, *J.*, 1888, **53**, 803). Here the powerful kationoid effect of the vicinal nitro-group presumably prevents electron abstraction by the chromium atom.

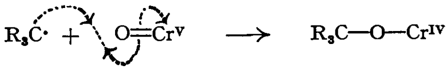
The chromium trioxide analogue of (IV) from diphenylmethane, *viz.*, (V), could not possibly split into hydrocarbon radicals capable of dimerisation, though such radicals might conceivably be derived from (III) or (VI). Since our previous work (Parts I and II) showed distinct evidence of some slight production of hydrocarbon radicals during the course of the chromium trioxide oxidation of diphenylmethane, we would suggest these might arise in the course of breakdown of a complex of type (III), or more probably of an earlier intermediate such as (VI).


(V.)



The active fragments (VII and VIII) resulting from the homolysis of the C–Cr link of (VI) would be produced in close juxtaposition, and the Franck–Rabinowitch concept of "primary recombination" would indicate that the changes (VI) ⟶ (IX) or (X) ⟶ (V) should, in the main, be intramolecular processes giving separated, *i.e.*, "free", radicals such as (VII), or transient chromium compounds such as (VIII) only as minor, concurrent, side products.

It may be pointed out that the odd electron shown in (VIII) cannot be regarded as a valency electron, but will have been absorbed at once into an inner shell of the chromium atom. It is rational therefore to depict the union of (VII) with (VIII) to give (IX) as a combination of carbon with oxygen upon which the electron-seeking chromium nucleus can gain complete control of still another electron, and approach more closely to its stable state of Cr^{III}, *i.e.*,



$$\text{R}_3\text{C}\cdot + \text{O}{=}\text{Cr}^{\text{V}} \longrightarrow \text{R}_3\text{C—O—Cr}^{\text{IV}}$$

This is similar to the mechanism which one of us (Waters, *Trans. Faraday Soc.*, 1946, **42**, 186) has suggested for the initial attack of chromium trioxide on C–H bonds, *viz.*

$$\text{R—H} + \text{O}{=}\text{Cr} \longrightarrow (\text{R}\cdot + \text{H—O—Cr}\cdot) \longrightarrow \text{H—O—Cr—R}$$

A possible explanation of the kinetics of the chromium trioxide oxidations of both diphenylmethane and triphenylmethane, which accords with knowledge of the Étard reaction, is therefore that the rate-determining process is the reaction of a molecule of chromium trioxide at each available C–H link of the hydrocarbon to give addition complexes of type (X), *via* (VI), which soon change over to rather more stable Cr^{IV} complexes of type (V) and are then broken down by water, or acetic acid, to the final oxidation products together with a mixture of a chromic salt and regenerated Cr^{VI}. Evidently this breakdown of the C–O–Cr^{IV} compounds must be slow, for otherwise our kinetic equation (*A*) would not hold.

The reaction of diphenylmethane and two molecules of chromium trioxide to give (X) or

(V) uses up *six* equivalents of Cr^{VI}. Of these *two* should be regenerated as Cr^{VI}, and *four* converted into Cr^{III} when (V) decomposes to yield benzophenone, but evidently in the period in which our *initial* rate determinations were measured only four equivalents (*i.e.*, 4/3 molecular proportions) of Cr^{VI} are locked up for each one which is finally converted into Cr^{III} when the complex mixture is poured into water.

At longer time intervals more extensive breakdown of the organo-chromium complexes must occur, for oxidation does not cease when the titre decrease $x = 0{\cdot}25a$, as equation (A) would suggest, but proceeds, though slowly, until x reaches a much higher value (*ca.* $0{\cdot}85a$). This late stage of the oxidation proceeds at a speed which approaches fairly closely that for a reaction of zero order (compare the graphs given in Part II), and this may well correspond with the gradual decomposition of the complex (V) with acetic acid, together with the reversible equilibria concerned with the locking up of some Cr^{VI} as the acetochromate $Cr^{III}(HCrO_4)(OAc)_2$.

We put forward these views, however, only in the form of speculative suggestions of which there appears as yet to be little possibility of proof.

EXPERIMENTAL.

Isolation of Chromic Acetochromate.—The substance to be oxidised (hydrobenzoin, diphenylmethane, or triphenylmethane) (0·2—0·5 g.) was dissolved in glacial acetic acid (10 c.c.) and 4 or 5 drops of a 5% solution of chromium trioxide in acetic anhydride were added with cooling. In the presence of an oxidisable substance only, a precipitate formed almost at once. This was collected on a sintered-glass filter, washed with acetic acid, then with carbon tetrachloride, and dried in a vacuum over potassium hydroxide and activated charcoal. It was a very hygroscopic chocolate-brown powder. Typical samples from different oxidations gave the following analyses: Cr (total), 37·7 (± 0·5), CrO_3, 35·2 (± 3·0); OAc, 36·0. $C_4H_7O_8Cr_2$ requires Cr (total), 37·4; CrO_3, 36·3; OAc, 41·2%.

Isolation of Chromic Acetoiodate.—The formation of an insoluble product was first observed during the addition of iodine to an oxidising mixture of diphenylmethane and chromic acid. It was shown not to contain the diphenylmethane moiety, and was subsequently prepared by the gradual addition, with cooling, of an excess of iodine in glacial acetic acid solution to chromium trioxide in the same solvent. The greenish-buff powder was collected on a sintered-glass filter, washed thoroughly with glacial acetic acid, and dried in a vacuum. It was insoluble in all common organic solvents, very sparingly soluble in cold water but freely soluble in hot water [Found: * Cr (total), 15·1; I, 39·9; IO_3, 54·9. $C_4H_6O_7ICr$ requires Cr (total), 15·1; I, 36·8; IO_3, 50·7%].

The *triphenylmethane–chromyl chloride complex* was obtained in over 90% yield by mixing equimolar proportions of triphenylmethane and chromyl chloride in purified carbon tetrachloride solution [Found: Cr (total), 12·9. $C_{19}H_{16},CrO_2Cl_2$ requires Cr, 13·0%].

Method of following the Initial Stages of the Reaction.—All initial rates were measured by mixing instantaneously known volumes of standardised reactants and, after measured time intervals, swamping the solutions by the addition of standard, freshly-prepared, potassium iodide in dilute sulphuric acid. The standardised chromium trioxide solution was first enclosed in a thin glass bulb immersed in the reaction vessel which already contained the hydrocarbon solution. After thermal equilibrium had been attained the bulb was broken so that the reactants mixed immediately. Reproducible results were regularly obtained, providing that the hydrocarbon was present in excess, but when less than 2 equivalents of hydrocarbon were taken then the titre decrease in 20-sec. intervals became too small for accurate measurement.

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