Tetrahedron, 1964, Vol. 20, pp. 1151 to 1161. Pergamon Press Ltd. Printed in Northern Ireland

ON THE MECHANISM OF THE OXIDATION OF HYDROCARBONS WITH CHROMIC ACID AND CHROMYL CHLORIDE[1]

K. B. WIBERG and R. EISENTHAL
Chemistry Department, Yale University, New Haven, Conn., U.S.A.

(*Received* 16 *September* 1963; *in revised form*, 21 *January* 1964)

IN A recent paper,[2] the mechanisms of the oxidation of hydrocarbons by chromic acid and chromyl chloride were reinterpreted. Some inconsistencies appear in the arguments given therein, and it is the purpose of this paper to review the data for the two related reactions, and the mechanistic conclusions which are permitted.

The facts concerning the chromic acid oxidation of hydrocarbons are as follows:

1. The relative reactivities of toluene, ethylbenzene, diphenylmethane and triphenylmethane in 91% aqueous acetic acid solvent are 1:3:6:3.[3] In 99% acetic acid, the relative reactivities of toluene, ethylbenzene and isopropylbenzene are 1:7·2:71.[4]
2. In the oxidation of aliphatic hydrocarbons, the relative rates of reaction at primary, secondary, and tertiary positions are 1:110:7000.[4]
3. The relative rates of oxidation of isobutane and 3-ethylpentane are 1:2·57.[4]
4. No anchimeric assistance is found in the oxidation of camphane,[4] isocamphane and cyclobutane.[5]
5. The rates of oxidation of cycloalkanes parallel the rates of solvolysis of the corresponding cycloalkyl tosylates.[5] The only exception was cyclobutane which reacted at a much lower rate than would be expected based on the rate of solvolysis of cyclobutyl tosylates.
6. In the oxidation of *p*-substituted diphenylmethanes, the value of the reaction constant ρ^+ is $-1\cdot17$.[3]
7. A kinetic isotope effect, $k_H/k_D = 6\cdot4$ at 30°, is found in the oxidation of diphenylmethane.[2] A kinetic isotope effect is also observed in the oxidation of aliphatic hydrocarbons, but the value is somewhat smaller.[6,7]
8. The oxidation of diphenylmethane and of other hydrocarbons is acid catalyzed, and the rate shows a first order dependence on both hydrocarbon and chromium (VI)[3,8] (not just $HCrO_4^-$ as in the alcohol oxidation).[9]

---

[1] This work was supported by grants from the Atomic Energy Commission and National Science Foundation.

[2] I. Necsoiu, A. T. Balaban, I. Pascaru, E. Sliam, M. Elian and C. D. Nenitzescu, *Tetrahedron* **19**, 1133 (1963).

[3] K. B. Wiberg and R. J. Evans, *Tetrahedron* **8**, 313 (1960).

[4] F. Mares and J. Roček, *Coll. Czech. Chem. Comm.* **26**, 2370 (1961).

[5] F. Mares, J. Roček and J. Sicher, *Coll. Czech. Chem. Comm.* **26**, 2355 (1961).

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

[7] K. B. Wiberg and G. Foster, *J. Amer. Chem. Soc.* **83**, 423 (1961).

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

[9] F. H. Westheimer and A. Novick, *J. Chem. Phys.* **11**, 506 (1943).

9. The oxidation of (+)-3-methylheptane led to (+)-3-methyl-3-heptanol with 75–80% retention of configuration.[7]

10. In the oxidation of 3-ethylpentane in glacial acetic acid in the presence of azide ion, the product was 3-ethyl-3-pentanol accompanied by 10% 3-ethyl-3-pentyl azide whereas in the oxidation of triphenylmethane 98% azide is found, and in the oxidation of 1,1-diphenylethane 51% azide is found.[10]

11. In the oxidation of neohexane, a major product is acetone.[4] The other product, pinacolone is formed with little skeletal rearrangement.[11]

The data may be interpreted as follows. The small difference in the reactivity between the compounds listed in (1), compared with the large difference in solvolytic reactivity of the corresponding halides (Table 1) indicates that the charge density at the carbon undergoing reaction is essentially unchanged in going from reactants to activated complex. On the other hand, the relative rates of oxidation are in good accord with the relative rates of hydrogen atom abstraction by reagents such as bromine atoms and trichlormethyl radicals (Table 1). The same conclusion is reached based on the small value of ρ^+ found for the reaction.[12]

Table 1. Relative reactivities in oxidation, hydrogen atom abstraction, and solvolysis

	Chromic acid oxidation		Hydrogen atom abstraction by		
Compound	91% HOAc[3]	99% HOAc[4]	CCl_3 Radicals[13]	Br Atoms[13]	Solvolysis of corresponding halides[14,15]
Toluene	1	1	1	1	1
Ethylbenzene	3·1	7·2	29	11	10^2
Isopropylbenzene		71	72	12	10^6
Diphenylmethane	6·3		29	7	10^5
Triphenylmethane	8·1		72	5·5	10^7

The difference in reactivity between the compounds listed in (2) may be interpreted in a similar way. Necsoiu *et al.*[2] quote the relative rates of solvolysis of alkyl bromides as $1:2\text{–}10:10^3\text{–}10^6$ and use this as a measure of the rate effects expected in heterolytic bond breaking. However, it is clear that the solvolysis of a primary halide is properly described as an S_N2 displacement process and that the rate of $CH_3Br \rightarrow CH_3^+ + Br^-$ is probably much lower than the rate of solvolysis. The relative rate 10^3 for tertiary halides is based on the use of ethanol as the solvent.

---

[10] I. Necsoiu and C. D. Nenitzescu, *Chem. & Ind.* 377 (1960).

[11] Cf. The discussion and experimental sections of this paper.

[12] Benzhydryl halide solvolysis leads to ρ^+ of −4 (H. C. Brown and Y. Okamoto, *J. Org. Chem.* **22,** 485 (1957); *J. Amer. Chem. Soc.* **80,** 4980 (1958). Hydrogen atom abstraction reactions are also best correlated with σ^+ but give values of ρ^+ from −0·75 to −1·5 (G. A. Russell, *J. Org. Chem.* **23,** 1407 (1958).

[13] G. A. Russell, C. DeBoer and K. M. Desmond, *J. Amer. Chem. Soc.* **85,** 365 (1963).

[14] A. Streitwieser, Jr., *Chem. Revs.* **56,** 571 (1956).

[15] The relative rates of solvolysis vary with solvent, and the available data are rather limited. The values given here are only approximate, but are probably a lower limit for an S_N1 process for benzyl chloride solvolysis undoubtedly has a considerable contribution from the S_N2 path.

The high nucleophilicity and low ionizing power of this solvent would be expected to lead to a small rate ratio. Even in a solvent of low nucleophilicity such as formic acid[16] the primary halide would be expected to react by an S_N2 mechanism. Here, however, we might expect to get a reasonable measure of the *minimum* rate differences between primary, secondary, and tertiary compounds. The rate ratios in this solvent are $1:26:10^8$.[14] The relative rates of oxidation are much lower.

On the other hand, the above authors quote the relative reactivities of primary, secondary and tertiary hydrogens in a hydrogen atom abstraction reaction as 1:4:7. This is the relative reactivity toward chlorine atoms, whereas the relative reactivities toward bromine atoms are 1:82:1640 at 127°, and are presumably even greater at 25°.[17]

Chlorination is unique among free radical hydrogen abstraction reactions in that it exhibits unusually low selectivity. This is seen, for example, in the very small difference in rate of reaction between cyclohexane and toluene whereas with most other hydrogen abstraction reactions, toluene is considerably more reactive than cyclohexane.[18] It seems reasonable to conclude that bromination is a better model for the free radical process than is chlorination, and it will be observed that the relative reactivities in chromic acid oxidation and in bromination are quite close.

The retention of configuration and lack of anchimeric assistance in the chromic acid oxidation gives clear evidence that the hydride ion abstraction process of the type

$$R_3C\text{—}H + O\text{=}CrO_3H_2 \rightarrow R_3C^+ \; HOCrO_3H_2^- \xrightarrow{H_2O} R_3COH$$

cannot be operative since this should lead to inversion of configuration in the oxidation of (+)-3-methylheptane and to rate enhancement in the oxidation of camphane, isocamphane and cyclobutane.

In further defining the mechanism, the data (3) and (5) are of particular interest. The change in rate of oxidation with hydrocarbon structure in each case parallels that observed in solvolytic reactions of the corresponding alcohol derivatives. The rate differences in the solvolyses are not due to electronic effects, but rather are due to the change in energy in going from the tetrahedral reactant to the trigonal activated complex, which results from changes in the geometry of the molecules. The similarity in rate behavior between the two types of reactions leads to the conclusion that the geometrical changes at the reacting carbon are similar in both reactions, and in turn this leads to the conclusion that the reacting carbon has a trigonal configuration in the activated complex for the oxidation.[5] The correlation in rate behavior between the two reactions would not be expected if the oxidation led to a pentacoordinate carbon arising from bidentate attack of chromic acid at the carbon-hydrogen bond.

All of these data lead to a picture of the mechanism of the reaction as one in which very little change in electron distribution occurs, and in which the reacting carbon goes from tetrahedral to trigonal. The following step must be a combination of the carbon with one of the oxygens of the intermediate chromium species which is formed in

---

[16] It should also be noted that formic acid is a better model for the solvent actually used in the oxidations—99% acetic acid—than is ethanol.

[17] P. C. Anson, P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.* 918 (1959).

[18] H. C. Brown and G. A. Russell, *J. Amer. Chem. Soc.* **74**, 3996 (1952); G. A. Russell and H. C. Brown, *Ibid.* **77**, 4578 (1955).

order to account for the retention of configuration. In structural terms, this may be written as

$$R_3CH + H_2CrO_4 \longrightarrow [R_3C\cdot\ H_3CrO_4]$$

$$[R_3C\cdot\ H_3CrO_4] \longrightarrow R_3C{-}O{-}Cr(IV)$$

$$R_3C{-}O{-}Cr(IV) \xrightarrow{H_2O} R_3COH + Cr(IV)$$

Here, the first step is hydrogen atom abstraction leading to the carbon radical and chromium (V) in the solvent cage. The combination of these species within the solvent cage has many analogies, and leads to the key intermediate, the chromium (IV) ester of the alcohol. The hydrolysis of such an ester has been shown to proceed with chromium-oxygen bond cleavage,[19] and the overall process would then lead to net retention of configuration.

Roček[20] has supported such a mechanism, but has proposed that the cage-bound intermediate should be written as a resonance hybrid:

$$[R_3C\cdot\ H_3CrO_4] \leftrightarrow [R_3C^+\ H_3CrO_4^-]$$

This may be the proper formulation, but since this intermediate appears after the rate determining step, it is not possible to obtain evidence either for or against the proposal.[21]

It appears to us that a more readily answered question is, what is the nature of the activated complex? For the oxidation of the aryl alkanes, in which very little difference in rate of reaction with a change in structure was observed, the activated complex may satisfactorily be described by the structures

$$[R_3C{-}H\ O{=}CrO_3H_2] \leftrightarrow [R_3C\cdot\ HO{-}CrO_3H_2]$$

and the contribution from structures such as

$$[R_3C^+\ HO{-}CrO_3H_2^-] \quad \text{or} \quad [R_3C^+\ H\cdot OCrO_3H_2^-]$$

(which are similar to those which have been written to explain polar effects in free radical reactions[12]) appear to be minimal. The contribution of such structures with the aliphatic hydrocarbons is more difficult to assess since good models for the relative reactivity in hydrogen atom and hydride abstraction processes are not readily available. All one can say is that these structures appear to have about the same contribution in chromic acid oxidation as in free radical bromination.

It should specifically be noted that the details of the transformation of the cage species to the chromium (IV) ester are not determined by the available data. It may

---

[19] K. B. Wiberg and G. Foster, *Chem. & Ind.* 108 (1961).

[20] J. Roček, *Tetrahedron Letters* 135 (1962).

[21] Roček's arguments for the proposal are: it would explain why the two species stay together long enough to recombine as is required by the observation of retention of configuration,[8] and it would account for the formation of carbonium ions in some reactions.[3,10] With regard to the first argument, it is known that cage recombination occurs to a considerable extent in the decomposition of azo-bis-isobutyronitrile in carbon tetrachloride (cf. C. Walling, *Free Radicals in Solution*, pp.7 6–79. J. Wiley, New York (1957). The viscosity of 90% acetic acid (20·5 millipoises) is considerably greater than that for carbon tetrachloride (9·0 millipoises, International Critical Tables, Vol. 5, p. 20; Vol. 7, p. 212), and this would make cage recombination more favorable in the acetic acid solvent than in carbon tetrachloride. The question of carbonium ion formation is considered later in the discussion.

very well proceed via initial electron transfer giving [R_3C^+ $Cr(IV)^-$] followed by internal return of this ion pair.

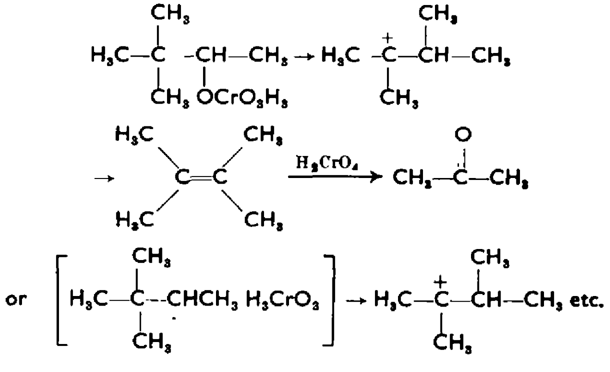
In the context of a mechanism of this type, how does one explain the results of the oxidation in the presence of azide ion? One must first remember that the reaction was carried out in glacial acetic acid as the solvent. If the reaction proceeds to the stage $R_3COCr(IV)$, what possibilities for further reaction appear? With an ester derived from a highly stabilized carbonium ion, carbon-oxygen bond cleavage may occur leading to the carbonium ion which may then react with azide ion to give the organic azide.[22] Alternately, if a highly stabilized carbonium ion may be formed, the reaction within the solvent cage may be

$$[R_3C\cdot\ H_3CrO_4] \rightarrow [R_3C^+\ H_3CrO_4^-]$$

which would lead to the carbonium ion directly. The relative yields of organic azide is directly related to the stability of the corresponding carbonium ion which is in accord with the above suggestions. The alcohol may be formed by the normal hydrolysis of $R_3COCr(IV)$ on addition of water to the reaction mixture, or may be formed by a reaction such as

$$R_3C\text{—}O\text{—}CrO_3H_3 \rightarrow R_3COH + H_2CrO_3$$

The final point to be considered is the oxidation of neohexane. The formation of acetone probably requires a series of reactions such as[4]



The neohexyl carbonium ion must be formed in the reaction either by a carbon-oxygen bond cleavage of an intermediate Cr (IV) ester, or by the direct electron transfer in the solvent cage. This would lead to 2,3-dimethyl-2-butene which is known to be oxidized by chromic acid to acetone.

There remains the possibility of the entire reaction proceeding via 2,3-dimethyl-2-butene, which could lead to pinacolone via the epoxide and a pinacol type rearrangement. 2,2-Dimethylbutane-4-C^{14} was prepared and subjected to the reaction. The pinacolone formed was degraded via hypobromide oxidation to pivalic acid and carbon tetrabromide. The latter was found to contain 95% of the label whereas the former had only 5·5% of the original activity. This indicates that no significant

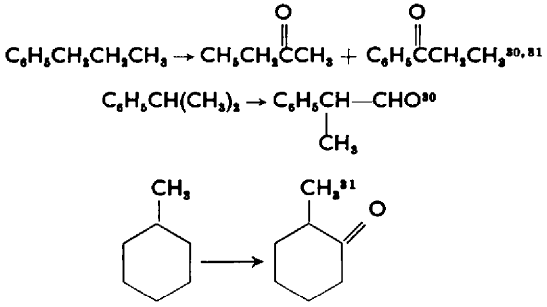
---

[22] Roček[30] has described this mode of reaction of the chromium (IV) ester as anomalous. However, it is well known that carboxylate esters of tertiary alcohols undergo solvolysis in acetic acid.[14] It might reasonably be expected that the chromium (IV) anion would be a better leaving group than the carboxylate anion.

skeletal isomerization occurred. The pinacolone must then arise from normal hydrolysis of the chromium (IV) ester followed by oxidation of the secondary alcohol to pinacolone or by oxidation of the chromium (IV) intermediate to chromium (V) followed by the loss of a proton. Even here, where both steric and electronic factors might be expected to favor cation formation, the alcohol is formed by a normal process.[23]

If the above may be accepted as a proper interpretation of the course of the chromic acid oxidation of hydrocarbons, we may turn to the question of the mechanism of the Étard reaction. Here, the available data are:

1. Most of the hydrocarbons which have been studied react with chromyl chloride in carbon tetrachloride or carbon disulfide solution to give an insoluble complex with the composition 1 hydrocarbon : 2 chromyl chloride.[2,24]
2. The relative reactivities of toluene, diphenylmethane and triphenylmethane are approximately 1:100:1000.[25]
3. The order of reactivity of aliphatic carbon-hydrogen bonds toward chromyl chloride is $3° > 2° > 1°$, although numerical values are not available.[26]
4. A change in dielectric constant of the solvent has a relatively small effect on the rate of reaction with toluene. Changing from carbon tetrachloride ($\epsilon = 2{\cdot}2$) to 1,2-dichloroethane ($\epsilon = 10{\cdot}1$) produced only a five-fold increase in rate.[27]
5. The Étard reaction of toluene and triphenylmethane showed a kinetic hydrogen isotope effect.[28]
6. In the oxidation of aliphatic hydrocarbons, a trace of olefin acts as a catalyst.[29]
7. The chromium in the Étard complex is in oxidation state 4.[2,26b]
8. Although the tertiary position is the most reactive, the products often appear to arise from attack at an adjacent position. For example:



$$C_6H_5CH_2CH_2CH_3 \rightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3 + C_6H_5\overset{\overset{O}{\|}}{C}CH_2CH_3{}^{30,31}$$

$$C_6H_5CH(CH_3)_2 \rightarrow C_6H_5\underset{\underset{CH_3}{|}}{CH}{-}CHO^{30}$$

---

[23] It may also be noted that the acetone had 92% of the expected amount of activity based on the above mechanism. Thus, for the most part, it is formed via 2,3-dimethyl-2-butene and not via a cleavage reaction of pinacolyl alcohol.

[24] W. H. Hartford and M. Darrin, *Chem. Revs.* **58**, 1 (1958).

[25] R. A. Stairs and J. W. Burns, *Canad. J. Chem.* **39**, 960 (1961).

[26a] C. C. Hobbs and B. Houston, *J. Amer. Chem. Soc.* **76**, 1254 (1954); [b] O. H. Wheeler, *Canad. J. Chem.* **38**, 2137 (1960).

[27] R. A. Stairs, *Canad. J. Chem.* **40**, 1656 (1962).

[28] I. P. Gragerov and M. P. Ponomarchuk, *Zh. Obshch. Khim.* **32**, 3568 (1962).

[29] A. Tillotson and B. Houston, *J. Amer. Chem. Soc.* **73**, 221 (1951); C. C. Hobbs and B. Houston, *Ibid.* **76**, 1254 (1954).

[30] W. von Miller and G. Rohde, *Ber. Dtsch. Chem. Ges.* **23**, 1356 (1891).

[31] K. B. Wiberg, B. Marshall and G. Foster, *Tetrahedron Letters* No. 8, 345 (1962).

9. When 1-phenylpropane-2,2-d_2 was treated with chromyl chloride, the ratio of benzyl methyl ketone to propiophenone decreased markedly, and the benzyl methyl ketone was found to have a deuterium in the benzylic methylene group.[31]

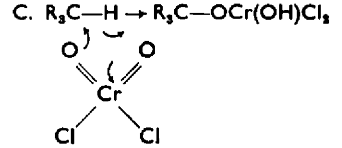
10. The ratio of benzyl methyl ketone to propiophenenone in the oxidation of propylbenzene is a function of the hydrocarbon: chromyl chloride ratio, going from 5·7:1 with a two-fold excess of hydrocarbon to 0·7:1 with a two-fold excess of chromyl chloride.[31]

11. A major by-product in the oxidation is the chlorinated hydrocarbon.[24,31]

Since a kinetic hydrogen isotope effect is observed, the rate controlling step must involve carbon-hydrogen bond breaking, leading to the following three possibilities.

$$\text{A. } R_3CH + CrO_2Cl_2 \rightarrow R_3C + HOCrOCl_2$$

$$\text{B. } R_3CH + CrO_2Cl_2 \rightarrow R_3C^+ + HOCrOCl_2^-$$



$$\text{C. } R_3C—H \rightarrow R_3C—OCr(OH)Cl_2$$

It is more difficult to distinguish between the possibilities here than with chromic acid oxidations because the data are so limited. If mechanism C is not operative with chromic acid, there seems to be little reason to expect that it would be operative with the structurally very similar chromyl chloride. However, it will be seen that the overall result of the first step is the same regardless of the mechanism actually involved.

The relative reactivity of toluene, diphenylmethane and triphenylmethane toward chromyl chloride (1:100:1000) is greater than that observed in chromic acid oxidation, but is still much less than that observed in solvolytic reaction. In particular, the small 2°:3° ratio is in marked contrast to the very large ratio observed in solvolysis. Although the relative rates of oxidation of aliphatic hydrocarbons by chromyl chloride are not known, data are available on relative reactivities toward chromyl acetate.[32] The similarity in the products of reaction by the two reagents and their structural similarity suggests that the chromyl acetate data will be a reasonable model for the relative rates of chromyl chloride oxidation. The rate ratio for secondary vs. tertiary carbon hydrogen bonds is only 1:20,[28] whereas the ratio of solvolytic reactivities of secondary and tertiary halides is about $1:10^6$.[14] Again, this suggests that the carbon undergoing reaction does not require a significant positive change on going to the activated complex.[33]

The data on the effect of solvent on the rate of oxidation of toluene cannot be interpreted using the available data. Unfortunately, the dielectric constant is not a useful measure of the ionizing power of a solvent.[34] A correlation with a parameter

---

[32] G. Foster and W. J. Hickinbottom, *J. Chem. Soc.* 680 (1960).

[33] It should be noted that the data indicate a primary C—H bond is about 10^{-8} as reactive as a secondary C—H bond. This large difference between primary and secondary positions coupled with the small secondary : tertiary ratio does not appear to have precedent among either free radical or carbonium ion reactions. It is possible that the reaction may involve a free radical chain and that reaction of the hydrocarbon radical with the solvent may markedly decrease the chain length in the case of primary groups. This possibility is receiving investigation.

[34] Cf. H. G. Grimm, H. Ruf and H. Wolff, *Z. Physik. Chem.* **B13**, 301 (1931).

such as Z[35] which is directly related to the ionizing power of the solvent would have been more useful. The data do not appear to be in opposition to a hydrogen atom abstraction.

The available data then suggest that process A is the correct one for the first step of the reaction. This may be followed by either E or F.

$$\begin{aligned} \text{E.}R_3C\cdot + HOCrO_2Cl_2 &\rightarrow R_3C\text{—}OCr(OH)Cl_2 \\ \text{or} &\rightarrow R_3CCl + HOCrOCl \\ \text{F.}R_3C\cdot + CrO_2Cl_2 &\rightarrow R_3C\text{—}O\text{—}CrOCl_2 \\ \text{or} &\rightarrow R_3CCl + CrO_2Cl \end{aligned}$$

and then

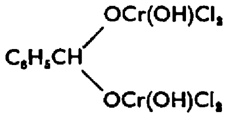
$$R_3COCrOCl_2 + R_3CH \rightarrow R_3COCr(OH)Cl_2 + R_3C\cdot$$

or

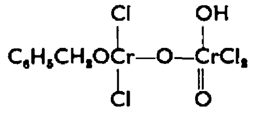
$$CrO_2Cl + R_3CH \rightarrow R_3C\cdot + HOCrOCl$$

In either case, it seems reasonable to expect that $R_3C\text{—}O\text{—}Cr(OH)Cl_2$ might be the first moderately stable intermediate.

The Étard reaction with toluene leads largely to benzaldehyde when the complex is decomposed under reducing conditions (as with aqueous bisulfite). Thus, the second mole of chromyl chloride must have reacted at one of the remaining carbon-hydrogen bonds giving



All of the available evidence appears to favor this structure, except for the data of Necsoiu *et al.*[2] who found that for an equal number of chromium atoms, the intensity of the ESR signal from the Étard complex was one-half that from a chromium (III) compound used as the standard. From this they concluded that half of the chromium atoms in the complex were paramagnetic, and half were diamagnetic, and suggested that the proper formulation for the Étard complex was:



$$C_6H_5CH_2O\overset{Cl}{\underset{Cl}{Cr}}\text{—}O\text{—}\overset{OH}{\underset{O}{Cr}}Cl_2$$

The fallacy in their argument lies in the fact that Cr^4 and Cr^3 do not have equal numbers of unpaired electrons. The magnetic susceptibility is a function of $S(S + 1)$ where S is the spin state. For Cr^3, $S = 3/2$ whereas for Cr^4, $S = 1$. The ratio of intensities in the ESR experiment for Cr^4 and Cr^3 should be 2/3·75 or 0·53 which is in good agreement with their experimental findings. Thus, the ESR experiment is in agreement with the argument that both of the chromium atoms in the Étard complex are in the +4 oxidation state, and is not in agreement with the previous conclusion.

Some uncertainty rests with the Étard complex derived from triphenylmethane. Hartford and Darrin[24] state that the complex involves only one chromyl chloride whereas the more recent work[2] indicates that two are involved. Further, the use of

---

[35] E. Kosower, *J. Amer. Chem. Soc.* **80**, 3253 (1958).

one and one-half equivalents of chromyl chloride led to a 90% yield of triphenylcarbinol.[36] Thus here, two equivalents of chromyl chloride are not required and the initially formed complex forms a complex with a second chromyl chloride if an excess is available.

It is interesting to note that whereas the decomposition of the complex from triphenylmethane with an aqueous medium gives triphenylcarbinol, the complex reacts with ether to regenerate triphenylmethane.[36] Apparently, the triphenylmethyl cation is formed during the decomposition, and it reacts with water to form the carbinol (as shown by oxygen-18 experiments)[36] or with ether to form the hydrocarbon, possibly via a hydride abstraction process. A process such as this may account for the observation that whereas the normal decomposition of the Étard complex from diphenylmethane gives benzophenone, the treatment of the complex with sulphur dioxide in glacial acetic acid gives benzhydrol.[2] Presumably a reduction has occurred in the latter case.

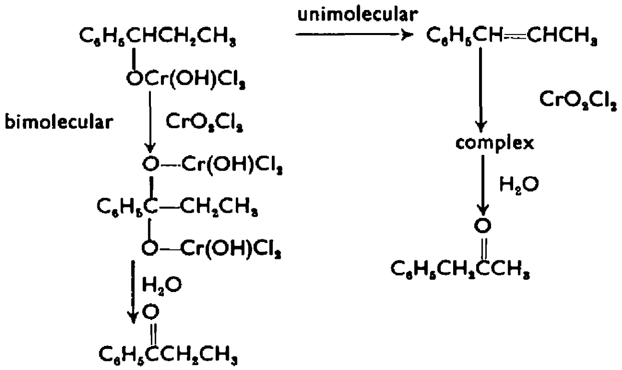
It has been suggested that the formation of benzyl methyl ketone in the Étard reaction results from the sequence[2]

$$[C_6H_5\overset{+}{C}HCH_2CH_3\cdot HCr_2O_4Cl_4] \rightarrow [C_6H_5CH_2\overset{+}{C}HCH_3\cdot HCr_2O_4Cl_4]$$

$$\xrightarrow{H_2O} C_6H_5CH_2CHOHCH_3 \xrightarrow{Cr^6\text{ aq.}} C_6H_5CH_2COCH_3$$

This type of sequence lacks merit for a number of reasons. Benzyl methyl ketone is the major oxygen-containing product even when the Étard complex is decomposed using aqueous bisulfite solution. The formation of benzyl methyl ketone in preference to propiophenone would require that the 1-phenyl-2-propyl cation would be formed in major amount from the benzylic 1-phenyl-1-propyl cation. Such a process seems inconceivable in view of the difference in stability of the two cations. The formation of benzyl methyl ketone would also require that the alcohol be oxidized by chromic acid at a rate which would effectively compete with the reaction of the latter with bisulfite. This is not correct. Further, any such scheme will not account for the change in product ratio in the oxidation of propylbenzene when the hydrocarbon:chromyl chloride ratio is changed.

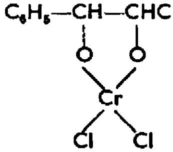
As we have pointed out previously,[31] the change in product ratio requires that the further reaction of the initial intermediate, R—OCr(OH)Cl_2, involve competition between two steps, one which is unimolecular and one which is bimolecular and involves chromyl chloride. The only way in which we have been able to formulate such a process is:



---

[34] L. V. Sulima and I. P. Gragerov, *J. Gen. Chem.* (*USSR*), **29**, 3787 (1959).

With a low concentration of chromyl chloride, the unimolecular path predominates and leads to benzyl methyl ketone. We have shown that the latter is the oxidation product of 1-phenylpropene, possibly via the intermediate



which could give the ketone in a pinacol type rearrangement. A hydrogen shift to the 1-position would occur as required by the deuterium labeling experiment. With an excess of chromyl chloride, the bimolecular path becomes important, leading to a "normal" Étard complex of the type formed by toluene. This on hydrolysis will give propiophenone. It should be noted that a similar view of hydrocarbon oxidation by chromyl acetate in acetic anhydride, i.e. that alkenes are commonly involved as intermediates, has been proposed by Foster and Hickinbottom.[32]

The observations that alkenes catalyze the Étard reaction of aliphatic hydrocarbons suggests that the oxidation of these compounds may be a free radical chain process with the alkene-chromyl chloride reaction generating some species which will initiate the reaction.

Finally, the oxidation of neohexane with chromyl acetate in acetic anhydride deserves some mention. Unlike the chromic acid oxidation, very little acetone is formed and the major product is pinacolone. Starting with 2,2-dimethylbutane-4-C^{14}, the pinacolone formed in the oxidation was degraded to pivalic acid and carbon tetrabromide. The pivalic acid was devoid of activity whereas the carbon tetrabromide had the full activity of the starting neohexane. Thus, no carbonium ion was formed at any time during this reaction. It seems probable that the same result will be obtained in the chronyl chloride oxidation although this experiment has not as yet been performed.

There are some aspects of the Étard reaction which still remain unclear, and we plan further experimental work designed to clear up some of the obscure points. However, we believe that the general course of the reaction is explained satisfactorily by the proposals given herein.

EXPERIMENTAL

3,3-*Dimethyl-2-butanone*-1-C^{14}. A solution of t-butylmagnesium chloride in ether (325 ml, 2·38 M, 0·77 mole) was added dropwise with stirring over a 3 hr period to 60·3 g acetyl-1-C^{14} chloride (0·77 mole, 0·34 mc) and 1·3 g cuprous chloride cooled to −60°. After addition, the mixture was stirred for 2 hr while the temp was allowed to increase from −70 to −40°. Saturated NH_4Cl aq. (200 ml) was added, the mixture allowed to warm to room temp, and 150 ml water added. The ether layer was separated and the aqueous layer washed with four 50 ml portions ether. The combined ether solution was washed with 50 ml portions sat. NaCl aq., dried ($MgSO_4$) and distilled through a 38 cm Vigreux column to remove most of the ether, the residue was distilled giving 54·1 g (70%) pinacolone b.p. 104–108°.

3,3-*Dimethylbutane*-1-C^{14}. To a solution of 60·5 g KOH in 250 ml distilled diethylene glycol was added 54·1 g pinacolone-C^{14}, 91·8 g hydrazine hydrate, and 130 ml diethylene glycol. The reaction mixture was stirred under N_2 and heated to reflux. Water was separated from the condensate using a Dean-Stark trap. After heating 5 hr, the solution was distilled giving a mixture of neohexane hydrazine and diethylene glycol. The organic layer was washed with 15 ml 1:1 hydrochloric acid–water until the aqueous extractant had a pH of 4 or less. The aqueous layer was washed with two

15 ml portions isopentane, and the latter was washed with 1:1 hydrochloric acid–water. The combined organic solutions were dried over K_2CO_3, and then $MgSO_4$. Some of the isopentane was removed through a small Vigreux column; the residue was distilled through a 28 plate spinning band column giving a 31·0 g neohexane (67%) b.p. 48·7–50·7°. Gas chromatographic analysis indicated no detectable amounts of impurities.

Oxidation with chromic acid in aqueous acetic acid. To a mixture of 111·8 g (0·375 mole) sodium dichromate trihydrate, 43·1 g (0·5 mole) neohexane-C^{14} (1·21 × 10^{-4} mc/mmole), 1425 g glacial acetic acid and 121·5 g water was added dropwise with stirring over a 2½ hr period, 147 g (1·5 mole) sulfuric acid. After 70 hr, 55% of the Cr^6 had been consumed. The reaction mixture was diluted with 3 l. ice-water and extracted with six 200 ml portions isopentane. The isopentane solution was washed with cold 10% NaOH aq. until neutral and then dried over Na_2SO_4. Most of the solvent was removed through an 11-stage Bruun column, and the residue distilled through a 38 cm Vigreux column until the head temp reached 32°. The residue was found to contain solvent, neohexane and pinacolone, and these were separated by preparative gas chromatography on Ucon-Polar at 100°.

The reaction mixture was also extracted with six 200 ml portions methylene chloride. The methylene chloride solution was treated as above giving a mixture of pinacolone and acetone. The mixture was separated by preparative gas chromatography.

The pinacolone (1·6 g) was stirred with a solution of 19·2 g NaOH and 12·8 g Br_2 in 64 ml water for 3 hr at 0–10°. The mixture was steam distilled until 200 ml water had been collected. The carbon tetrabromide was collected by filtration giving 3·5 g (68%). After sublimation, it had an activity of 1·15 and 1·11 × 10^{-4} mc/mmole (duplicate analyses).

The pot residue from the steam distillation was acidified with 30 g H_2SO_4. Silver sulfate (31 g) was added and the Br_2 was removed from the cooled mixture under red. press. Finally, 15 ml 30% hydrogen peroxide solution was added and the mixture was steam distilled until 200 ml water had been collected. The distillate was treated with NaOH aq. to a pH of 10, and the water was removed using a rotary evaporator giving 1·25 g sodium pivalate.

The salt was dissolved in water and 3 drops conc. HCl, 3·06 g *p*-bromophenacyl chloride and 30 ml 95% ethanol were added. After heating to reflux for 1 hr, the solution was cooled and filtered giving 3·0 g *p*-bromophenacyl ester. A portion was recrystallized twice from 95% ethanol (m.p. 74–76°) and had an activity of 6·80 and 6·79 × 10^{-6} mc/mmole.

The acetone formed (2·07 g) was converted to the 2,4-dinitrophenylhydrazone (m.p. 123·5–125·5°) and had an activity of 5·63 and 5·51 × 10^{-5} mc/mmole.

Oxidation with chromyl acetate in acetic acid–acetic anhydride. To a solution of 83·3 g (0·83 mole) CrO_3 in 200 ml acetic anhydride and 300 ml glacial acetic acid was added with cooling and stirring during ½ hr, 43·1 g neohexane-C^{14} (6·59 and 6·63 × 10^{-5} mc/mmole) in 100 ml glacial acetic acid. After 40 hr, titration indicated 94% consumption of Cr (VI). One liter of water and 5 drops conc. H_2SO_4 were added and the mixture was allowed to stand 3 hr. The solution was then worked up as for the preceding oxidation. The isopentane solution contained a small amount of neohexane, pinacolone, and another ketone having about the same retention time as methyl isopropyl ketone. The two ketones were formed in a 14:1 ratio with pinacolone predominating. The methylene chloride solution contained pinacolone, acetone and a small amount of an unidentified compound. The carbon tetrabromide formed in the degradation of the pinacolone had an activity of 6·85 and 6·94 × 10^{-5} mc/mmole; the *p*-bromophenacyl ester of pivalic acid had no observable activity; and the acetone had an activity of 1·66 and 1·67 × 10^{-5} mc/mmole. The low activity of the acetone indicates that all of it cannot have been formed via tetramethylethylene; possibly some arises from a cleavage reaction of pinacolyl alcohol or a derivative of this alcohol. This might lead to the t-butyl cation which would lose a proton and be further oxidized to unlabeled acetone.